UNIVERSITY OF NORTHERN COLORADO

Greeley, Colorado

The Graduate School

A STUDY TO MAXIMIZE THE LEARNING EXPERIENCE

IN THE PHYSICAL CHEMISTRY LABORATORY

A Dissertation Submitted in Partial Fulfillment
of the Requirements for the Degree of

Doctor of Arts

Ronald Edward Watras

College of Arts and Sciences

Department of Chemistry

Summer 1979

AFIM-CI- **REPORT DOCUMENTATION PAGE**

| | READ INSTRUCTIONS BEFORE COMPLETING FORM |

1. REPORT NUMBER	2 GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
79-224D	AD-A101 502	

4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED
A Study to Maximize the Learning Experience in the Physical Chemistry Laboratory	THESIS/DISSERTATION
	6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s)
Ronald Edward Watras	Doctoral Thesis

LEVEL II

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
AFIT STUDENT AT: University of Northern Colorado	

11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE
AFIT/NR WPAFB OH 45433	1979
	13. NUMBER OF PAGES
	340

14. MONITORING AGENCY NAME & ADDRESS(If different from Controlling Office)	15. SECURITY CLASS. (of this report)
	UNCLASS
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

APPROVED FOR PUBLIC RELEASE: IAW AFR 190-17

23 JUN 1981

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

DTIC
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

ATTACHED

81 7 16 023

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DEAN OF THE GRADUATE SCHOOL

_____

Examination Date on Dissertation_____

ABSTRACT

Watras, Ronald Edward. "A Study to Maximize the Learning
    Experience in the Physical Chemistry Laboratory."
    Published Doctor of Arts dissertation, University
    of Northern Colorado, 1979.

This study was conducted to: (1) develop and evalu-

ate a set of curriculum materials designed to teach physical

chemistry concepts in a laboratory setting, a portion of

which was designed to teach those concepts exclusive of the

lecture part of the course, and (2) design the materials to

maximize the learning experiences in the laboratory.

An extensive review of the literature showed that

although there have been efforts to improve learning

abilities in many areas of chemistry, little or no evidence

has been found in improving students' learning abilities

in the physical chemistry laboratory.

The materials were implemented, continually

evaluated, and revised based on oral and written evaluations

of the students, oral and written evaluations of the

instructors, and oral and written evaluations of the major

adviser. This process was repeated through four revisions.

As part of the evaluation process, student questionnaires

were analyzed at the end of each fall, winter, and spring

quarter starting in the fall of 1976 and ending in the

spring of 1979. Another part of the evaluation was the

use of ACS examination questions to determine the effectiveness of the materials.

Student response to the materials was very favorable, but the results of the ACS testing was not as favorable. From these two factors, it was concluded (paraphrasing Bent 1975) that this study tried to improve learning in a physical chemistry laboratory setting and in trying to improve learning, learning was improved.

ACKNOWLEDGMENTS

I am thankful to the many people who have helped me throughout this study:

To my wife, Margaret, for her understanding, sacrifices, and assistance throughout this work and graduate studies.

To my major advisor, Dr. M. Lynn James, for his guidance, inspiration, and assistance during my graduate work.

To the United States Air Force including the United States Air Force Academy and the Air Force Institute of Technology for sponsoring my research.

To all other individuals who aided me during this research.

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CHAPTER I

INTRODUCTION TO THE STUDY

This study includes the construction and validation
of a set of curriculum materials designed to teach certain
physical chemistry concepts with little or no reinforcement
from a lecture setting. These materials (Appendixes A-R)
represent more than just experimental procedures as are
found in most of the common physical chemistry laboratory
textbooks (Bettelheim, 1971; Brennan and Tipper, 1967;
Crockford et al., 1965 and 1975; Daniels, et al., 1956 and
1970; Oelke, 1969; Salsberg, et al., 1969; Shoemaker and
Garland, 1962; Steinbach and King, 1950; and Wilson, 1968).
The materials were designed to develop the students' higher
cognitive skills; i.e., understanding, problem solving,
comprehension, application, and critical thinking; and to
relieve the instructor in the lecture portion of the course
from treating certain topic areas. The following section
identifies the need for the development of such materials
and outlines some of the previous research that has been
conducted.

Background

The goals of science education are different today
than they were twenty years ago. Hobey (1966) says that in

the past it was demanded that students memorize facts, laws, and theories. Today more emphasis is placed on the students' understanding of the discipline being studied. Anderson says not only is there a need for new perspectives for teaching science, but

> It is especially important that we develop new perspectives for laboratory instruction in science. It is a widely accepted credo that experiences in the laboratory are essential to effective science programs. Occasionally this tenet is questioned, however, and, although laboratory experiences survive, the answers offered critics are not over-whelmingly impressive. Certainly laboratory work is not as efficient and effective a mode of instruction as it might be, and it is high time that we take a hard look, with a fresh perspective, at learning in the laboratory (1976, p. vi).

Defining the Study

In this study a set of curriculum materials designed to teach physical chemistry concepts in the laboratory were developed. To accomplish this goal several steps were taken including adding sections to existing physical chemistry experiments as used by the chemistry department at the University of Northern Colorado (UNC). These added sections include:

1. A study guide and review questions, i.e., an outline of things to be accomplished prior to coming to lab

2. Key words, i.e., new terms, equations, and symbols that the student should be able to define prior to performing the laboratory experiment

3. Objectives, i.e., performance that the student should be able to demonstrate after completing the lab

4. Preliminary report, i.e., a series of short questions that the students must answer before coming to class

5. References and supplementary readings

6. Examples and problems, i.e., materials to reinforce the learning process

Each of these sections will be discussed in more depth in chapter IV.

A second aspect of the study dealt with the development of three new physical chemistry experiments. These experiments were also designed to teach physical chemistry concepts in the laboratory, and they also contained the sections just listed.

Purposes of the Study

1. To develop a set of curriculum materials designed to teach physical chemistry concepts in the laboratory

2. To revise existing physical chemistry experiments and make them more effective instructional devices

3. To develop new physical chemistry activities designed to teach physical chemistry concepts

4. To develop a set of curriculum materials designed to increase higher cognitive skills of the students

Significance of the Study

With this study as an example, chemical educators could modify other laboratory experiments to help their students maximize their learning experience in a laboratory setting.

Procedure

This study represents research which began in the summer of 1975 and was completed in the summer of 1979. In preparation for this study the following educational systems

were reviewed:

1. Instructional objectives

2. Instructional systems

3. Individualized instruction

4. Behavioral objectives

5. Goal analysis

6. Experimental design

7. Instructional materials

8. Questioning techniques

9. Learning taxonomies

10. Measuring achievement

The review of these educational systems was accomplished through normal course work and individualized course work at UNC.

In the summer of 1975 an extensive computerized literature search was conducted on laboratory activities in physical chemistry using the ERIC Clearinghouse. The analysis of the literature search indicated that the present study was indeed original.

Further preparation was made by teaching a year of physical chemistry laboratory classes at the United States Air Force Academy under the supervision of professors D. Seegmiller, A. Fannin, and L. Smith. This teaching assignment was an invaluable experience because it allowed the author to perform the duties of a physical chemistry laboratory instructor and become thoroughly acquainted with materials typically used in physical chemistry laboratories.

This study consists of eighteen activities (Appendixes A-R). The experimental portion of this study began when the first draft of an activity (Appendix A) was prepared incorporating the items as listed in the Defining the Study section. This activity was used in both the summer and fall of 1976 in the physical chemistry laboratory classes at the University of Northern Colorado. The major adviser critically reviewed this activity. The teaching assistant noted any problems in teaching from this activity, such as not enough examples. The students were asked to give constructive criticism relative to this activity by means of student questionnaires. Based on the suggestions of the students, the teaching assistants, and the major adviser, this activity was then revised. Subsequent revisions involved a similar process. The students' suggestions were obtained from the analysis of questionnaires distributed at the end of each quarter.

Except for the last two activities (Appendixes Q & R) all activities were used and revised at least two additional times. All the activities except the last activity (Appendix R) were performed by the students at UNC and revised based upon this implementation. The last activity was revised after being performed by the students at the United States Air Force Academy (USAFA).

Early in the fall of 1976 a preliminary questionnaire was mailed to selected chemistry departments throughout the country (Appendix S). The main purpose of this

questionnaire was to ascertain the feasibility of developing a new laboratory curriculum for physical chemistry. The results (Chapter III) were very encouraging. Furthermore, the majority of the professors responding felt that their physical chemistry laboratory course was inadequate. The author, aided by this feedback, prepared other activities, used them in the classroom, revised them, and used them again.

One of the objectives of the present study was to teach certain areas of physical chemistry in the laboratory without discussing them in the regular lecture classes. This was tried and evaluated with activities in the area of electrochemistry (Appendix F). As will be explained in chapter III, the students' cognitive skills were measured by the use of questions obtained from standardized American Chemical Society (ACS) examinations in the area of electro-chemistry. The scores in electrochemistry were also compared with the scores in other areas of thermodynamics. The other areas in thermodynamics were taught in the lecture portion of the course as well as in the laboratory.

Another objective of this study was to develop new activities and experiments in physical chemistry. Three of these new activities dealt with topics not commonly found in most physical chemistry laboratory textbooks. They included the following activities:

1. A unit on data analysis and treatment of errors (Appendix A)

2. The preparation of an extensive review of the literature in a specified area, e.g., "Ammcnium cyanate-urea conversion," in the area of kinetics (Appendix O)

3. The preparation of a computer program in the area of quantum mechanics, e.g., "The treatment of a particle in a one-dimensional box," (Appendix Q)

4. A new experiment "Determination of Transference Numbers by the Moving Boundary Method," (Appendix P)

5. A new experiment "The Photoelectric Effect," (Appendix R)

The appropriateness of this study was evaluated again in the spring of 1979 when another computerized literature search was conducted. The analysis of this literature search indicated that the present study was still a timely topic.

Limitations

1. The activities must be of such a nature so as not to require the use of expensive and very specialized apparatus

2. The activities, by necessity, must be developed, implemented, revised, and used again limiting the total number of activities which can be developed

3. There was no control group due to the small size of the physical chemistry classes

Assumptions of the Study

Two major assumptions were made in this study. The first is that the students participating in this study are representative of physical chemistry students thoughout the country. The second is that the colleges responding to the questionnaire (Appendix S) are representative of colleges throughout the country.

Summary

To a set of existing physical chemistry experiments other materials were developed and added. The main purpose of these materials was to teach physical chemistry concepts in the laboratory. The following is an outline of the remaining chapters.

Chapter II, <u>Review of the Literature</u>, will present background theories, ideas, and studies concerned with the teaching of chemistry.

Chapter III, <u>Evaluation</u>, will present the results of the questionnaires and critique sheets used in this study. The results of the American Chemical Society (ACS) tests that were used to evaluate a part of this study will also be provided.

Chapter IV, <u>Discussion of Materials and Suggested Use</u>, will include a review and use of the materials by the teacher and student.

Chapter V, <u>Conclusions and Recommendations</u>, will present the conclusions made as a result of the study as well as recommendations for further study.

CHAPTER II

REVIEW OF THE LITERATURE

This literature review is divided into three sections: (1) Innovations in Undergraduate Chemistry, (2) Innovations in Physical Chemistry, and (3) Physical Chemistry Experiments. The review focuses on previous research in these areas and identifies the need for continuing educational research in physical chemistry and physical chemistry laboratory courses. This is especially true in the area of physical chemistry laboratory since little if any research in this area could be found in the literature.

Innovations in Undergraduate Chemistry

In their book on innovations, Unruh and Alexander say that there were many innovations in curriculum development in the sixties. They state the following:

> Sputnik's orbiting of the earth in 1957 is generally credited with triggering the curriculum reform movement. Leadership in the beginning of the movement came from university professors in the academic disciplines. . . .
> Although schools were slow to adopt the new curriculum programs in the first years following Sputnik, by the end of the decade the curriculum reforms had probably reached more American schools than any of the other innovations in education. . . . (1970, p. 55)
> What are the major changes in science education?

The old science programs usually relied on a single textbook that emphasized factual information, sometimes in such extensive encyclopedic treatment that students were overwhelmed. Most textbook authors organized the information around classification. A laboratory manual was usually provided to students, but laboratory work in science tended to be after-the fact verification (1970, p. 59).

Anderson says that these innovations were necessary to keep up with the burgeoning topics being forced on the schools by colleges and universities (1976). Hobey says that elementary and high schools have been asked to teach concepts that were formerly taught in high schools and colleges respectively. Hobey goes on to say:

. . . we notice that more and more theory is being pushed lower and lower in the curriculum, going sometimes into even the high school chemistry courses. . . The disconcerting aspect of this push of theory into the earlier levels of education is that it pushes out the descriptive material it is supposed to be explaining. The earlier theory is introduced, the fewer real cases the student has to tie and apply it to, and the less meaningful the theory becomes (1966, p. 610).

Thus, elementary and high school teachers have been forced to modify their curriculum. They strive to present concepts which challenge but do not overwhelm. They give students the opportunity to explore, to make mistakes, and to reflect on their experiences.

In the seventies there have been efforts in the teaching of general college chemistry and general college chemistry laboratory courses. Day and Houk (1970) wrote,

The need for improved teaching in general chemistry has been long recognized. Most efforts . . . have centered attention on the content and structure of the course or on the use of various audio-visual aids. . . . The most important single factor in

> this course is the detailed outline of what the
> student must know (be able to do) in order to pass
> the course, (p. 629)

i.e., behavioral objectives. Thus, they proposed a student

paced learning course in general chemistry.

Humphreys (1971) describes another so called

innovation in which he combined individualized instruction

with audio-visual methods and called it a tutorial system.

The heart of his audio-visual system is a "teacher operated

TV recording facility." (p. 277) Humphreys reports that

> Response was enthusiastic, particularly when the
> material was broken into short (e.g., 20 min) units
> and included brief diagnostic tests. . . .
> With the development of such centers, the role
> of the lecture can change so that it becomes in-
> creasingly a medium for stimulating interest and
> focusing attention on important areas (p. 278).

White et al. (1972) described a modified self-paced

approach to the ceaching of a freshman level chemistry

course,

> . . . commonly attributed to Keller and often
> referred to as a 'Personalized System of
> Instruction,' (PSI). In this method the emphasis
> is on self-pacing, strong student-instructor
> interaction, and individual understanding of each
> course topic (p. 772).

White was one of the first to report on the use of the

Keller Plan in chemistry. Since his report in 1972, there

have been many other reports on the use of the Keller Plan

in chemistry courses. A summary of some of these reports

continues in this section.

In the first of two papers Lewis and Wolf (1973)

reported on the implementation of the Keller Plan in their

small freshman chemistry class of betwen 15-30 students.
The study guide for each of nineteen units consisted of
sections similar to those advocated in this study in
Chapter I. They reported that grades were assigned as
follows:

> A student who completed all nineteen units was
> guaranteed at least a B grade in the course, subject
> to satisfactory completion of the laboratory program.
> Completion of 16 units rated a C, and 12 units a D-,
> the minimum passing grade (p. 51).

Of significance to the present study, the laboratory was the
same as for non PSI students.

In their second paper Lewis and Wolf (1974) reported
on the results of their Keller Plan courses. The most
significant finding was that PSI students who continued on
with organic chemistry after completing a PSI version of
freshman chemistry did as well as non PSI students. They
also reported that organic chemistry was offered in a PSI
format as well as the traditional lecture-laboratory format.

In 1973 Leo reported on the results of a Keller Plan
as tried in his large freshman chemistry class. He stated
that students obtained more A's and B's than previous
students. He further stated that the "Laboratory (p. 50)
experiments are conducted in usual manner, except open lab
is also made available to enhance the self-paced approach."

A correlation between American College Testing (ACT)
scores and American Chemical Society (ACS) scores in a PSI
general chemistry course was reported by Vandenbroucke
(1975). He stated that "The test results show that the

students in the PSI sections are learning at about the same level as those students of comparable ability in the lecture sections." (p. 518)

A slightly different approach was reported by Shakhashiri (1975). He used computer generated but ungraded quizzes. These were scored by the computer and diagnostic reports were prepared for each student. However, the major examinations and the laboratory were the same as those in most freshman chemistry courses in this country.

Most of the cases of "innovation" that have been reported in the literature dealt with efforts to change the lecture portion of the course. However, in most of these cases reported in the literature there was no significant difference in the methods used in the laboratory. One exception was that of Cassen and Forster (1973) who reported about a one semester laboratory course for nonscience majors in which the students' grades were based on how many laboratory activities were completed. The laboratory was self-paced, but activities were not considered complete until a student passed a laboratory quiz on that unit. The questions were analogous to the problems incorporated in this study, i.e., the purpose was the same, reinforcement of the learning process.

A different approach was taken by Livant (1975) in generating an organic laboratory course. The object of the course was to have students design and perfect "Ideal Lab" experiments, i.e., those that "impart chemical creativity,

as well as lab technique, since good labwork requires both thinking and doing." (p. 452) This approach was incorporated in a slightly different way as shown in appendixes O and Q of this study.

Innovations in Physical Chemistry

As pointed out by Hobey (1966, p. 607) the content in all areas of physical chemistry "has been doubling every eight or ten years. Teachers . . . in their zeal to better train the undergraduate have introduced more and more physical chemistry . . . into the undergraduate curriculum." If this is true, then the amount of material has more than doubled since 1966. This has forced much of what used to be taught in physical chemistry into other cources, or has caused the instructor to omit some of the material in part or altogether. Hobey said:

> We may be fast approching the stage where a student
> knows all about the bonding in the naphthalene molecule
> but would never recognize napthalene in the odor of
> mothballs (p. 610).

Today teachers in some countries are making general chemistry more descriptive as it once was and one teacher in Italy suggests that:

> As far as the physical chemistry teaching is concerned,
> it seems clear that a considerable improvement could be
> achieved by developing a three-year teaching of physical
> chemistry beginning from the 2nd year of the degree
> course. A complete reorganization of the corresponding
> laboratory courses also appears necessary, which should
> lead to a better coordination with the theoretical
> courses, to the elimination of out-of-date experiments
> and to the inclusion of more modern ones, possible of
> the integrated type (Mazzucato, 1976, p. 6).

In the United States a number of studies have been conducted on teaching physical chemistry using a Keller type of approach. Most of these studies are discussed in this section of the study. In the first, Bent suggests that "Lecturing is commonplace not because it is effective but because it is easy." (1974, p. 661) Bent has modified the Keller Plan approach for physical chemistry by retaining two lectures a week, using the same laboratory, but adding a tutorial center where students have two attempts to pass each weekly exam.

In a second article Bent (1975) gives some statistics on his Keller type physical chemistry course. After his analysis he found that the performance was about the same as it was in past traditional courses.

Kestner and Kestner (1973) describe a true Keller course in physical chemistry. As is true in general chemistry courses it contained objectives, study questions and sample problems. The means for obtaining a particular grade were explained at the start of the course. In this approach the activities included the traditional laboratory experiments which were performed in the traditional way except that they were self-paced. Kestner and Kestner reported that

> Very often our students do poorly because they have not mastered the fundamentals before they are asked to apply them (p. 61).

To some extent this very problem was addressed in this study.

In two papers Kemp (1974 & 1975) analyzed a self-paced course he developed for teaching physical chemistry. As a result of his course he has written a self-paced textbook in physical chemistry (1974) based on the activity packages that he developed for his course. One achievement was the construction of a set of self-paced packages for petroleum engineering, chemical engineering, and geology majors who were required to take physical chemistry.

Besides the Keller courses, other things that have been done include having students produce videotapes in the physical chemistry laboratory as one of their assigned experiments. The students videotaped actual physical chemistry laboratory experiments while they were being performed by other students. Rouda (1973) initiated the video-production to alleviate the problem of explaining how to perform an experiment when every student is performing a different experiment due to a limited amount of each type of apparatus. The students preview the videotape at their own convenience prior to performing the experiment.

Contract grading is not new in many high school and college courses, but Schufle considered it an innovation when he reported the use of contract grading in physical chemistry (1972). The class agrees to certain minimum standards and for a higher grade students list other activities that they will accomplish. Reportedly the students try harder since "the compulsion is self-imposed, not imposed by the instructor." (p. 255)

Combs (1976) compared two approaches to physical chemistry for different semesters during the same school year. In the first semester he taught the traditional way. In the second semester he still presented formal lectures, but they were videotaped so that students could listen to them again at their own convenience. In addition, he gave eight examinations instead of four with the provision that any exam could be taken early if the assigned homework problems were completed. If a student received a grade less than 90 he had to retest at the scheduled time. The students were given only a partially completed outline for the course, and they had to devise their own study guide. Combs reported that the course average was sixteen percentage points higher the second semester, but there was no comparison made c individual grades.

At the 174th ACS National Meeting in Chicago, Pollnow (1977) described a problem-oriented, tutorial course in physical chemistry. He emphasized three things:

1. Learning is effective repetition

2. Learning is problem solving

3. The burden of learning must reside with the learner

At the same meeting, Watras and James (1977) presented a preliminary report on learning physical chemistry concepts in a laboratory setting. It is the most comprehensive study in the literature that addresses innovations in the area of physical chemistry laboratory.

Physical Chemistry Experiments

In the literature, especially the Journal of Chemical Education, there are new updated experiments which can be performed in the physical chemistry laboratory (Coe and Nibler 1973, Wise 1972, Frankel and Wise 1973, Norris, Broadbent and Davies 1973, and Rouda 1973). But as Rouda (1973, p. 126) reported:

> The amount of apparatus is often limited in upper-level physical chemistry courses in universities with small enrollments, and the students are required to perform the experiments on a rotating schedule.

There are some fairly simple things that can be done with existing experiments to improve them. For instance, one can update existing experiments, e.g., Atomic Emission (Appendix M) by including current readings from the literature (Hansch et al., 1979). One can suggest practical applications of an experiment, e.g., relating adsorption to environmental problems such as oil spills (Illustrated World of Science Encyclopedia 1971). Similarly, as suggested by Trumbore (1975) one can take student concerns into consideration when performing some experiments.

Other applications include the use of computers to simulate experiments that for one reason or another cannot be performed in the laboratory, or to perform the calculations required in a given experiment (Wise 1972, Frankel and Davis 1973, and Norris et al., 1973).

Summary

A review of the literature indicates that innovations are being developed in the areas of physical chemistry, but for the most part the innovations are an extension of studies done in the area of general chemistry, i.e., PSI or the Keller Plan. Little progress has been reported in updating chemistry instruction in the laboratory other than to say it must take place (Mazzucato 1976). Thus, this literature review indicates that physical chemistry instruction in the laboratory has not been modified, but has been taught the same traditional way for many years.

CHAPTER III

EVALUATION

Chapter III includes the findings of this study.
The first section of the evaluation includes the results of
the chemistry departmental college survey (Appendix S). The
next section contains a summary of the student questionnaires
(Appendix T), and a short discussion on the revision of the
learning materials. The third section of this chapter con-
tains the statistical findings related to the American
Chemical Society (ACS) standardized examination. Within
this section the data are analyzed to seek evidence for the
validity of the learning materials. The chapter concludes
with a brief section on some general comments and suggestions
of the students.

Chemistry Departmental Questionnaire

In order to determine which concepts and principles
are the most important in a physical chemistry course and
in order to help establish the validity of the learning
materials, a comparison was made of a majority of the
published physical chemistry and physical chemistry labora-
tory textbooks (Selected Bibliography). Additionally, a
questionnaire was mailed to thirty-one colleges and
universities to obtain information on their physical

chemistry laboratory courses. The introductory letter, a list of the colleges and universities (hereafter referred to as colleges), and the questionnaire are in appendix S. The results of this survey are also in appendix S (Part 4) with a short summary in this section.

Twenty-six (84%) of the thirty-one colleges responded. Seventy-three percent of those responding said that their physical chemistry laboratory was a separate course from the physical chemistry lecture course. However, 40% of the laboratory courses were for one semester or less.

Seventy-three percent of the colleges used one of the major published laboratory texts, but supplemented the text with additional materials. Twenty percent used supplementary materials designed by their own faculty, twenty percent used experiments from the Journal of Chemical Education, and twenty percent used modifications of experiments from the laboratory textbooks. The other forty percent used eight other types of materials. Those not using one of the standard laboratory texts used their own written materials based on experiments in the standard laboratory textbooks.

Twenty-one of the respondents replied that they were satisfied with their materials. One of the respondents replied that he was not satisfied with the textbook and material he was using. Only three respondents replied that they were very-satisfied with the materials that they were using. One respondent did not reply to this question. In

the two extreme cases, i.e., the very satisfied and the
dissatisfied, the instructors used a standard laboratory
textbook and supplementary materials.

Fifty percent of the respondents replied that in
no case should physical chemistry concepts be taught
exclusively in the laboratory. Two of the respondents
replied "Yes," and two of the respondents said "Perhaps."
The others gave qualified answers (Appendix S, Part 4).

In response to the question, "How could P-chem
laboratory be made more effective?", there were eighteen
different replies. They are listed in appendix S (Part 4).
Noteworthy was the fact that ten respondents were dissatis-
fied with budget allowances for physical chemistry labora-
tory. Yet only five respondents replied that they would
like to see an improvement in curriculum materials.

A comparison was made on the number of experiments
performed at both the University of Northern Colorado (UNC)
and the USAF Academy (USAFA) with those performed at the
colleges responding to the questionnaire. This comparison
indicated that more experiments were performed at UNC and
USAFA than at the colleges responding to the questionnaire.
In addition, the number of experiments performed at these
colleges varied from a minimum of 5 experiments per term,
to a maximum of 15 experiments per term. The total number of
experiments varied between a minimum of 5 experiments to a
maximum of 20 experiments.

Selection of the colleges was made in part on the following basis:

1. Five of the colleges were selected because they, as UNC, offered the Doctor of Arts (DA) degree in chemistry

2. Seven of the colleges were selected because the author was acquainted with an instructor at those colleges

3. Five of the colleges were selected because the major adviser had an acquaintance at those colleges

4. The University of Wyoming and six of the colleges in Colorado were selected because of their proximity to UNC

5. The remaining eight colleges were chosen at random

Part of the rationale for selecting the colleges on the above basis was to increase the number of questionnaires that would be returned. The local colleges were chosen so that the author could visit their chemistry departments to obtain a more in-depth understanding of their programs. In fact, one of the questionnaires was completed on such a visit to a local college that had not returned it.

The initial findings of the college questionnaire were presented at the 174th National Meeting of the American Chemical Society in Chicago (Watras and James 1977). A number of the participants offered their suggestions and helped to provide a rationale for continuing the study.

Student Questionnaires

Appendix T contains samples of the questionnaires completed by the physical chemistry students at UNC. These questionnaires were given at the end of the unit on

electrochemistry and at the end of each quarter term. Since these questionnaires are based on the course content, it is necessary to outline the organization of the laboratory course and list the modifications added to the experiments.

In the first quarter of the three quarter physical chemistry laboratory course the students spent three weeks on the fundamentals of programming a Monroe 1655 programmable calculator (the class met for 3 hours once a week), three weeks on the analysis and treatment of data (Appendix A), and four weeks on experiments in thermodynamics (Appendixes B, C, D, and E). The first thermodynamics experiment (Appendix B) was not modified. The remaining three thermodynamics experiments were modified before the students received them. The initial modifications included the addition of: (1) a list of objectives, (2) a preliminary report, (3) a reference section, (4) an expanded theory section, (5) solved-example problems, and (6) additional unsolved problems which also served as a post test. These modifications were later expanded to include: (1) a study guide and (2) a list of key words. A discussion of how to use these materials is presented in chapter IV.

As previously stated, the student questionnaires were one of the factors taken into consideration in revising the materials used in this study. The results are listed in appendix T, but a short summary of the results are presented here. Question number one compares the modified experiments with the unmodified experiment. The students said that the

unmodified laboratory reports were more time consuming and harder. They also said that the modified experiments: (1) were better developed theoretically, (2) dealt with the topic more directly, and (3) the problems helped in understanding the laboratory experiment.

The purpose of question number three (Appendix T, Part 2) was to determine whether or not the error treatment unit helped students calculate the error associated with their results. Fifty percent of the students said the unit on error analysis prepared them sufficiently. Twenty-five percent of the students stated that they wanted to see more examples and problems dealing with error analysis.

In question number four the students were asked what did they find the most valuable in their lab write-up. Most of the students stated that the examples and problems helped give them a better understanding of physical chemistry concepts. This response was also evident in the fifth question, in which students requested that more problems than originally present be included in the modified experiments. In addition, 90% of the students were of the opinion that the modified experiments taught physical chemistry concepts in a laboratory setting. However, some students suggested that this objective could be better met if there were fewer experiments and more time to concentrate on the theory.

When asked if the laboratory part of the course complemented the lecture part of the course, seventy-five

percent of the students said that the modified experiments did complement the lectures. But 50% of the students also said that they felt that lecture and laboratory did not have to complement each other.

The responses to the first questionnaire were used in revising and further modifying the following three experiments:

1. Adiabatic calorimetry (Appendix C)

2. Calorimetric Measurement of Heats of Neutralization (Appendix D)

3. Chemical Equilibrium (Appendix E)

The comments of the teaching assistants and the research adviser were also used in revising the materials. The unmodified experiment served as a control device, since the other thermodynamics experiments were compared to it. In the opinion of the students, physical chemistry concepts were more readily learned using the modified experiments than the unmodified experiment.

In order to determine whether or not a physical chemistry concept could be learned exclusively in the laboratory, a unit on electrochemistry was presented in the laboratory without any discussion of the material in the lecture portion of the course. Two types of evaluations were used to determine if physical chemistry concepts could be learned solely in the laboratory. The first type of evaluation was another questionnaire (Appendix T, Part 3) on the electrochemistry unit. The second type of evaluation consisted of questions on electrochemistry concepts taken from

from the 1968, 1969, 1973, and 1976 versions of the ACS

Cooperative Test in Physical Chemistry. The results will

be discussed separately in the next section. Because of the

restrictive nature of the test, it is not included

in the appendix, but is available for viewing through the

research advisor.

The questionnaire was used not only to get student

feedback, but again to evaluate the affective domain. In

their book, "Measuring Pupil Achievement and Aptitude,"

Lindvall and Nitko state:

> . . . the teacher should be vitally concerned with the
> attitudes and interests of students, even though they
> will probably have to be assessed through informal,
> nonobjective procedures. But such procedures can be
> very useful. Certainly a teacher can investigate stu-
> dents' interests by talking with them, by listening to
> them, and by observing their actions. Such information
> can greatly help teachers to judge the effectiveness of
> their other teaching procedures and materials and,
> therefore, to plan pupil activities (1975, p. 44).

The results of the second student questionnaire are given

in appendix T (Part 4) with a brief summary of the results

given in this section.

The first question used Likert-type responses to

determine how the student felt about the unit on electro-

chemistry concepts. Sixty-three percent of the students

said the unit was satisfactory. Only 18% of the students

said the unit was unsatisfactory. The others were undecided

or said that the unit was better than just satisfactory.

The next three questions (Appendix T, Part 3) had

yes-no responses so that the student could answer quickly

but answer with a definite opinion. In response to the
second question, "Was it necessary to include electro-
chemistry as part of the overall P-chem course?" All the
students thought that the unit was necessary. The third
question asked, "Would you have learned as much about electro-
chemistry concepts if only a lecture presentation had been
given and no laboratory activities?" Eighty-one percent of
the students felt that they would not have learned as much.
Finally, the fourth question asked, "Did this set of experi-
ments try to teach electrochemistry concepts?" All the
students felt that it did.

The last three questions on the electrochemistry
questionnaire were open-ended. They asked how the materials
should be revised. The responses were helpful to the author
in revising the materials. One student's response was
particularly noteworthy in that it reflects one of the
objectives of this study. "The Laboratory write-ups force
me to explore the ideas behind electrochemistry instead of
just memorizing equations and terminology."

The third questionnaire (Appendix T, Part 5) was
completed at the end of the winter quarter. All of the
questions were open-ended. Most of them were similar to
questions asked on the first two questionnaires in that
they asked just about the same questions, but over different
activities. The responses were also similar in that most
of the students wanted even more problems included in the
materials and all students thought that the laboratory was

achieving the goal of teaching physical chemistry concepts.
However, many students complained about the amount of time
required for a one hour credit per quarter course.

The discussion of the responses to the questionnaires
that have just been presented was based on the originally
developed materials. Very similar questionnaires were given
to new students to complete after each of the subsequent two
revisions. The responses of the students were similar in
that they felt as did the previous students that physical
chemistry concepts can be learned and were learned in a
laboratory setting. They felt that the addition of an ex-
panded theory section, and an examples-and-problems section
helped them to learn physical chemistry concepts more effec-
tively. However, the students became more critical with each
revision. Some of their criticisms are discussed in the last
section of this chapter. Most of them are listed in
appendix T (Part 6).

The last questionnaire of the year (Appendix T,
Part 6) was completed by the students at the end of the
spring quarter. Besides including general criticisms which
are to be discussed at the end of this chapter, the question-
naire included a specific question about a different type of
physical chemistry project. The students were assigned a
project involving a literature search and the preparation
of a review paper on an assigned topic based upon the
literature search. The first and last year of this study
the search involved kinetic reactions. The second year of

this study the   search involved concepts in quantum mechan-
ics. In general, for all three years 83% of the students
thought that the literature search project was worthwhile.

ACS Evaluation of the Students'
Learning of Electrochemistry

In an attempt to evaluate cognitive learning in
electrochemistry, twelve questions on electrochemistry
concepts were gathered from the 1968, 1969, 1973, and 1976
versions of ACS standardized tests. All the questions based
on electrochemical principles were used, but duplicate
questions of which there were three were used only once.
These twelve questions were given to the students at the end
of the winter quarter of 1978. Electrochemistry concepts
were presented in the laboratory during the first three weeks
of the winter quarter. At the end of the winter quarter, a
forty-five question ACS Cooperative Test in Physical Chemis-
try, Subtest I--Thermodynamics, Form 1973 was also given to
the physical chemistry students. Four of the forty-five
questions were electrochemistry problems. They were graded
as part of the thermodynamics test and as part of the
electrochemistry test. The results of these two tests are
shown in table 1. The percentile scores were determined
from the information supplied by ACS and contained in
appendix U.

TABLE 1

ACS THERMODYANMICS TEST

WINTER QUARTER 1978

Student #	Thermodynamics Test			Electrochemistry Test
	Raw Score Right	National %-tile	% Right	% Right
1	23	60	51.1	33.3
2	23	60	51.1	41.7
3	18	28	40.0	8.3
4	17	20	37.8	25.0
5	16	15	35.6	33.3
6	18	28	40.0	33.3
7	19	35	42.2	33.3
8	15	15	33.3	33.3
9	21	45	46.7	25.0
10	13	6	28.9	25.0
11	16	15	35.6	33.3
Mean		29.7	40.2	29.5
Std. Dev.		18.5	7.1	8.6

In analyzing the results of the two tests, it can be seen that the students performed about ten percentage points better on the general thermodyamics test than on the questions on electrochemistry concepts. (If the score for student #3 is dropped, the difference is only 8.5 percentage points.)

The results indicate the learning that occurred did not occur to the degree which was desired. However, it should be noted that, except for one student, the learning that occurred was greater than that which can be statistically predicted for an individual making random guesses on a 4-item multiple-choice test. Additionally, the results indicate that although the students performed better on the general thermodynamics test, that performance (except for two students) was still below the fiftieth percentile as measured by ACS standards. Thus the low scores on the electrochemistry examination should be interpreted in light of the scores on the general thermodynamics test.

At the end of the winter quarter of 1979, the same twelve questions were used to test the students' knowledge of electrochemistry concepts. Ten other questions chosen by the instructor of the course were gathered to test concepts covered during the other laboratory classes. The results of these tests are shown in table 2. The forty-five question ACS test was given much earlier in the quarter and was, therefore, not used for comparison purposes.

As can be seen in table 2, three of the students performed better on the electrochemistry test, seven of the students performed better on the other concepts portion, and two performed the same on both portions of the test. However, the questions on the other concepts portion of the test were directly related to concepts that were covered in the laboratory and to some extent in the lecture portion of the course.

TABLE 2

ANALYSIS OF LABORATORY TESTS FOR

WINTER QUARTER 1979

Student #	Electrochemistry Test	Rest of Labs
	% Right	% Right
1	33.3	50.0
2	25.0	60.0
3	58.3	80.0
4	41.7	40.0
5	41.7	40.0
6	75.0	80.0
7	50.0	70.0
8	33.3	20.0
9	33.3	80.0
10	25.0	50.0
11	58.3	70.0
12	50.0	60.0
13	41.7	80.0
Mean	43.6	60.0
Std. Dev.	14.5	19.1

The electrochemistry questions were taken from the ACS standardized tests so that no bias could be introduced. In fact, at least two of the questions were on concepts not specifically covered in the laboratory. Furthermore, if those questions are dropped, the mean score of the students taking the course in the winter of 1979 increases to 44.6%.

By ACS standards, if a student gets half the questions right on an ACS standardized examination, it can be considered to be a good indication of his having mastered the concepts on which the standardized test was based.

The results of these evaluations indicate that one of the purposes of this study, to teach physical chemistry concepts solely in a laboratory setting, was not met. Thus this study suggests that the teaching of concepts in both lecture and laboratory, as would be expected, is more successful than teaching them solely in the laboratory.

General Student Comments and Suggestions

The last two questions on the questionnaire IV asked the students to evaluate the physical chemistry laboratory course for the whole year. They were asked to describe some of the successes and some of the failures. Finally, they were asked for suggestions on improving the laboratory portion of the course. The comments are listed in appendix T. These comments are from students who took the physical chemistry laboratory course in 1977-78 and 1978-79.

An analysis of these comments shows that many of the comments are contradictory. For example, one student said that the laboratory portion of the course was good in that it demonstrated the application of principles discussed in the lecture portion of the course, while another student said that the physical chemistry experiments were not always pertinent. A student said that he complained a lot, but he thought he learned a lot due to the extra effort required,

while another student said that he had not learned anything from the laboratory portion of the course. Another example dealt with the literature search in which one student said that the literature research paper was definitely worthwhile, while another student said the literature search was a waste of time.

Some common suggestions were (1) to cut down on the number of laboratories and laboratory reports, and spend more time on learning the concepts, (2) the instructor should have the laboratory ready to go, and (3) do something about the equipment problem.

This chapter may best be summarized by quoting from an article by Henry Bent on a self-paced physical chemistry course:

> You can't win. For every acquisition there is an equivalent loss. Every aspect of teaching is burdened with features antithetical to it. The charming thing about our enterprise, however, is that with a constructive attitude, . . . you can improve, and in trying to improve YOU CAN'T LOSE. The well-intended opposite of good—if imperfect—thing is usually a good—if imperfect—thing. Mutual antagonism and consequent reconciliation is the constant, recurrent path to perfection (1975, p. 448).

CHAPTER IV

DISCUSSION OF MATERIALS AND SUGGESTED USE

This chapter includes the following information:

1.   A short discussion on additions and modifica-
tions that have been made to the physical chemistry
laboratory experiments

2.   Comments on using the materials

3.   A discussion on each of the new experiments
developed for use in a physical chemistry laboratory class

The above information will be discussed in separate sections

of this chapter.

Additions and Modifications

The following additions and modifications have been

added to all the experiments included in the appendix to

this study except the one experiment (Appendix B) as was

mentioned in chapter 3.

1.   A study guide

2.   A list of objectives

3.   A list of key words

4.   A preliminary report

5.   A reference section

6.   An expanded theory section

7.   Solved-example problems

8.   Additional unsolved problems

The newly-developed experiments include these additions and modifications. The main purpose of these additions and modifications is to help the students learn some physical chemistry concepts on their own while they perform experiments. With these changes, it is the author's aim to have the students learn basic principles, applications, and problem solving skills, i.e., higher cognitive skills. Each of these additions and modifications is discussed below.

Study Guide

The first addition and modification, the study guide, was not originally included when the first draft of the modified materials was developed in the summer of 1976. During the first quarter of use, the fall of 1976, some students asked for more specific information to prepare them for the assigned experiment and the result was the development of a study guide. The purposes of the study guide are: (1) to assign materials to be read and problems to be worked out from their physical chemistry textbook; (2) to remind the students to read the theory and procedure sections, to supply definitions for the key words, and to complete the preliminary report; and (3) to advise the students of any special problems of which they should be aware. The reading assignments and the problems to be worked out were originally keyed to the students' textbook by referring to pages and problems in their text. However, in this present form the

references to the readings are more general so that the
student can find them in any edition of any physical chem-
istry textbook. The problems are written out in the study
guide itself. Ideally, the students will follow the study
guide. By doing the activities outlined in the study guide,
the student begins learning physical chemistry concepts in
the laboratory.

Objectives

The second modification involved the addition of a
list of objectives. Day and Houk said:

> The most important single factor in this course
> (student-paced general chemistry course) is the detailed
> outline of what the student must know in order to pass
> the course. . . . A clear statement of objectives should
> always be worked out (1970, p. 629).

The student should read the objectives and keep them in mind
while studying the material.

Key Words

A third addition included the list of key words, or
terms. In this section each student is asked to supply
written definitions for the terms. Also, the student should
be able to relate the term to the symbol(s) for the term
that is most prevalent in the literature. Finally, if
possible, the student is asked to supply an equation or
equations related to the term. The list of key words serves
two purposes: (1) the key words give the students some idea
about the content included in the experiment, and (2) the
key words help the students learn some physical chemistry

concepts on their own. Many of the key words are defined within the theory section of the laboratory package. However, the students are expected to define the key words in their laboratory report even if they are not in the theory section. Defining terms is a lower cognitive skill, but this should help the students develop their higher cognitive skills, because they will have a better understanding of basic principles.

Preliminary Report

One of the major problems with many laboratory courses is that the students come to the laboratory unprepared to do the experiment. As a result they have a difficult time performing the experiment and leave the laboratory feeling that they have learned nothing. The next modification required the students to complete a preliminary report which is designed to alleviate this problem. The purpose of the preliminary report was to require the student to read the theory and procedure sections prior to class. The instructor can determine if this has been accomplished by having the student turn in the preliminary report or by giving an unannounced quiz such as the one in appendix V. A similar procedure has been used at the USAF Academy for the last two years. The student must pass an individualized computer generated quiz before he is allowed to commence work on his laboratory experiment. In their verbal and written critiques some of the students at UNC specifically suggested

that the procedure outlined above be continued because it helped them to learn physical chemistry concepts.

Reference and Supplementary Readings

Each set of the laboratory materials contains a reference section, which serves two purposes. The first purpose is that it provides suggested references for those students who need a more detailed explanation of the theory than is given in the theory section. Secondly, many of the examples and problems included in the modified experiments need to be cited and the reference section provides for that need.

Prior to the theory section there is a concise list of apparatus and chemicals. This section is beneficial to both the instructor and student since it enables them to be prepared to begin the experiment. It also serves as a reminder to the instructor of the solutions and the equipment which should be prepared prior to beginning the lab.

Theory

The theory is in the next section. It is not intended that the theory section be an all inclusive treatise about the underlying principles upon which the experiment is based. Rather, the basic principles are given upon which the student can build when writing the laboratory report. The equations used are developed along with the theory rather than simply provided for the students.

After the theory section there is the traditional procedure section. In some experiments there is also a section outlining any calculations to be done and a data sheet on which the students can put their data and results. These sections were part of the original materials at UNC.

Examples and Problems

One of the most useful sections according to the responses of the students is that of the solved-example problems. Ideally, the students should try working through the example problems prior to looking at the solutions. This will indicate to the student whether he understands the concepts involved. If the example problems are approached in this way, it may not even be necessary for the student to work the unsolved problems. *If the student does have trouble* with the example problems, he can study the solutions, reflect on the examples, and then go back and try to solve an unsolved problem.

The unsolved problems should also be approached in a special way. It is suggested that the student actually try working each problem assigned by the instructor. <u>Not all the problems need to be assigned</u>. In fact, other problems may be substituted. The purpose of these problems is to help the student learn physical chemistry concepts. Kemp says to the students in his self-paced physical chemistry textbook:

> Don't try to take short cuts. Learning physical chemistry is not the easiest task in the world. It, like other technical subjects, takes several readings and a large investment of time in solving problems.

If you expect it to be easy you are in the wrong course (1974, p. P-3).

Recommendations on How to Use the Materials

This section will provide a short review of the materials contained in appendixes A--N. Some suggestions for using the materials to help teach the concepts are also contained in this section. These suggestions are based on use of the materials from the summer of 1976 through the spring of 1979.

Data Analysis and Treatment of Errors

The first set of materials, data analysis and treatment of errors, is contained in appendix A. The student should already be familiar with the topics discussed in the first eight pages of these materials from previous chemistry courses. These topics are significant figures, mean, standard deviation, and rejection of data. The instructor should review these topics and insure that the student is able to work the first four problems pertaining to these topics. Finally, the instructor should give a review test over this material.

When this packet was written, it was intended that this important topic, data analysis and treatment of errors, be covered only in the laboratory class. One way that this was accomplished was to have each student take a specific concept and explain it to the class. The first year each

student in addition to explaining a concept also wrote a quiz question and an approved solution for his concept.

Another topic, the propagation of errors of derived results, is one of the most important concepts that the students will need in writing physical chemistry laboratory reports. The instructor should slowly review this concept with the students. The class should work through the four example problems step by step. Then the students should work through the unsolved problems independently, asking for help if they need it. The instructor should stress that the student will be responsible for including this same type of error treatment for most of the laboratory experiments performed in physical chemistry for the rest of the year.

The last topic contained in this set of materials includes graphical techniques, curve fitting techniques, and some techniques for transforming an equation into an equation of a straight line. All of these techniques will be needed throughout the year.

In addition to having problems distributed throughout this set of materials, there are a number of problems at the end of the packet in the form of a self-test. It is strongly suggested that the instructor also provide some form of evaluation of the concepts learned in this set of material.

Determination of the Molecular Weight of a
Volatile Substance: The Victor
Meyer Method

This experiment (Appendix B) was the first physical
chemistry laboratory experiment performed at UNC in the fall
of 1976 and 1977. It was not performed in the fall of 1978.
This experiment was performed without the additions and
modifications that were discussed in this chapter. Because
it was performed this way, a comparison was made between
this experiment and the three modified experiments which
were performed in the fall of 1976 and 1977. The results
of this comparison were discussed in chapter III. Because
this experiment remained unmodified, there are no accompany-
ing suggestions for the instructor.

Adiabatic Calorimetry

This experiment (Appendix C) was one of three
modified experiments performed by the students at UNC in
the fall of 1976, 1977, and 1978. This was one of the
favorite experiments of the students because when performed
correctly the students' results are in good agreement with
those found in the literature. This experiment involves
the use of a Parr bomb calorimeter. Furthermore, this
experiment teaches one of the basic concepts in thermo-
dynamics, that the heat content is directly proportional to
the amount of substance.

Before the experiment is performed, the instructor
is advised to give a short quiz based on the preliminary

report and the procedure sections. Then the instructor is advised to carefully demonstrate the entire procedure to the students. Finally, the instructor should review the safety precautions given for this experiment.

The instructor is also advised to discuss the units used in this experiment. The author feels that it is important that the students be able to work the problems included in this experiment using a variety of units. Thus, the solved-example problems include units for energy such as the calorie as well as the joule, which is the prescribed unit in the international system of units (SI).

Calorimetric Measurements of Heats of Neutralization

In this experiment (Appendix D) the student computes the heat of ionization of a weak base from the experimentally determined heat of neutralization and the value for the heat of ionization of water. To do this experiment with good results, the student must be careful when using the apparatus.

Problems with the apparatus caused some student results to be less accurate than desirable. A typical problem is that when the stopper is inserted into the metal tubing the fit is either too loose and the stopper comes out prematurely or the fit is too tight and the stopper can't be forced out. The instructor should advise the students of this potential problem. In any case, the concept of heat of neutralization is reinforced by the examples-and-problems section which has been added to the experiment.

Chemical Equilibrium

The apparatus used in the chemical equilibrium experiment (Appendix E) was cited in the Journal of Chemical Education in 1935. Although old, the concepts presented in the experiment are just as important today as they were in 1935. In this experiment the student determines the equilibrium constant, K_p. Since K_p is mathematically related to the change in Gibbs free energy, ΔG^O, through the relationship $\Delta G^O = -RT\ln K_p$, the student can calculate ΔG^O.

Prior to performing the experiment, the instructor should stress that the students must be careful when using the specially constructed glass apparatus. In addition, the instructor should insure that the students are aware of the toxic nature of the gaseous system, $N_2O_4 = 2NO_2$, just in case the glass apparatus should break. The instructor should point out that this experiment provides an excellent review of thermodynamic concepts. Finally, time permitting, the instructor should review the relationship between the degree of dissociation and K_p.

Electrochemistry Unit

This unit, consisting of three experiments, is contained in appendix F. As explained previously, the main purpose of this unit on electrochemistry is to teach physical chemistry concepts exclusive of any coverage in the lecture portion of the course. To do this successfully requires some work on the part of the instructor.

The following represents a suggested procedure to be used by the instructor. This procedure was a result of observations by the author, the teaching assistants, and the students when this experiment was being implemented during the winter quarters of 1977, 1978, and 1979. Many potential problems can be avoided if the instructor follows these suggestions and encourages the students to follow the study guides that accompany each experiment.

Experiment #5

1. At the start of the class the instructor should plan a half-hour discussion on the following topics: (a) Faraday's laws, (b) equivalent weights, (c) balancing redox equations, (d) key words, and (e) electromotive series and standard reduction potential

2. The calomel half-cell should be allowed to stand for a couple of days in order to equilibrate

3. The main purpose of the agar, if used at all, is as a quick setting gel to help hold the paste in place

4. The instructor should prepare a sample cell or show the class samples of cells constructed in a previous year as an example of cell construction

5. Give the class the approximate E^o value for a decinormal calomel cell, 0.33 volts

6. The instructor should show the class different types of cells, e.g., Daniell, dry, etc.

Experiment #6

1. The instructor should plan a 15 minute review on the Nernst equation and thermodynamic relationships

2. The instructor should ask the class why they are not dealing with a standard hydrogen electrode

3. Prior to performing the experiment, the instructor should tell the students that they should be prepared to set up the apparatus from Figures 6-5 and 6-7

4. The instructor should tell the class to design an appropriate data sheet

5. The instructor should remind the students to take the barometric pressure reading

6. The instructor should give the students a short quiz at the start of the class, if time permits

Experiment #7

1. The instructor should present a 15 minute review on pH and activities

2. Since the students will need most of the laboratory period to perform the experiment, no other material will be covered

Adsorption of Acetic Acid by Charcoal

This experiment (Appendix G) is another favorite of the students. Not only are the students' results good, but this experiment has practical applications. If desired, the concept of adsorption can readily be taught in the laboratory portion of the course with little emphasis by the instructor in the lecture portion of the course.

The following are some suggestions for the instructor to assist in teaching physical chemistry concepts applicable to this experiment:

1. Since quite a bit of glassware will be used, the instructor should check to see that all necessary glassware is available prior to the start of the laboratory period

2. Be aware that the students will need 0.500$\underline{N}$ acetic acid and 0.100$\underline{N}$ NaOH, standardized solutions, and activated charcoal granules

3. The instructor should review with the class how to rearrange an equation into one having the form of a straight line

4. The instructor should discuss practical applications, e.g., current environmental problems of how to clean up oil spills

5. The instructor should review the key words with the students, especially absorption versus adsorption

Surface Tension

The experiment on surface tension (Appendix H) is an experiment that the students can be motivated to enjoy. To do this there are a number of demonstrations that the instructor can perform. Two examples are:

1. Dipping different wire shapes into a soap solution and discussing the surfaces formed

2. Demonstrating capillary action and discussing practical applications

In addition, the instructor should review with the students the key words and demonstrate how to use the tensiometer. Surface tension, like adsorption, is ideally suited to teach in a laboratory setting.

Binary Solid-Liquid Phase Diagram

This was an experiment (Appendix I) that the students did not like. One reason was that they had difficulty determining where the breaks occurred on their cooling curve. Another reason that the students had difficulty was because a month had elapsed since the materials had been discussed in the lecture portion of the course. If this delay occurs the laboratory instructor might take the time to review the main concepts, especially the Gibbs Phase Rule.

Rate and Order of a Chemical Reaction

This kinetics experiment is contained in appendix J of this study. Because of the quantity of theory in the area of kinetics, it would be impossible to summarize the concepts adequately. For this reason the student is referred to his textbook. In addition, the concepts involved are so complex, so varied, and so numerous, it is not recommended that this experiment be performed until after being discussed in the lecture portion of the course. The author recommends that this experiment be performed after the experiment on conductivity (Appendix K) has been completed since the kinetic experiment uses the conductivity apparatus and the skills learned in the conductivity experiment. It is also suggested that the students be given a short quiz over the preliminary report and procedure sections prior to starting the experiment.

Conductance of Strong and Weak Electrolytes

This is another experiment (Appendix K) that could be used to teach physical chemistry concepts in the laboratory without the necessity of teaching these concepts in the lecture portion of the course. To have the students learn physical chemistry concepts in the laboratory, it is important to have a short discussion period prior to performing the experiment. This discussion should include how to set up a Wheatstone bridge circuit.

This experiment integrates many of the important

concepts the student has had in physical chemistry since the beginning of the year. Thus, the instructor should remind the students that they have previously learned about concepts such as degree of dissociation and strong electrolytes. The instructor should also inform the students that unless they are careful and unless they make their adjustments slowly, they may have problems determining the null point.

Refractive Index

Refractive Index (Appendix L) is one of three experiments that has been performed by the students in the area of quantum chemistry. The concepts in this experiment are conducive to being learned in a laboratory setting. The students should not have difficulty with this experiment if the instructor demonstrates how to use the refractometer. The addition of the solved-example problems should be of help to the student in performing the calculations required for this experiment.

Atomic Emission Spectra

This quantum chemistry experiment (Appendix M) is the second of three experiments that have been performed by the students at UNC during the winter quarter of 1977 and the spring quarters of 1978 and 1979. This experiment is not time consuming; however, it includes the basic concepts of quantum mechanics. These concepts include the relation-ships between wavelength, wave number, frequency, and the change in energy that an electron in an atom can undergo.

The examples and problems contained in this experiment reinforce the learning of these concepts. However, it is suggested that the instructor make an additional reading assignment from related articles in the literature such as the article by Hansch, Schawlow, and Series entitled "The Spectrum of Atomic Hydrogen" (1979).

Acid Dissociation Constant of Methyl Red

This experiment (Appendix N) also contains concepts related to quantum chemistry. Different solutions have a maximum absorbance at different wavelengths. One characteristic of many indicators is that their solutions exhibit more than one color depending on the pH of the solution. Since the absorbance at some wavelength is proportional to the concentration. Beer's law can be used to find the concentration ratios. From the concentration ratios and the pH, the pK of the solute can be calculated.

This is a time-consuming experiment, but the instructor should still take laboratory time to lead a short discussion of the concepts to be learned in this experiment. One method that has been successful is to have each of the students present a review of one of the concepts to the class. In addition, the instructor should remind the students to study the examples and problems at the end of the experiment for help in performing the required calculations.

A Review of New Materials and
Suggestions for Their Use

This section reviews the new materials and experiments that were developed for a physical chemistry laboratory course. One set of materials, data analysis and treatment of errors, is not new but was greatly expanded. It has already been discussed at the beginning of the previous section entitled, Recommendations on How to Use the Materials. The purpose and suggestions for using each new set of materials or experiments are included in this section.

Literature Search

A type of activity other than a laboratory experiment was implemented in the physical chemistry laboratory course at UNC in the spring of 1977. The students were given the assignment to perform an extensive literature search in the area of chemical kinetics (Appendix O). The topics were chosen from Frost and Pearson's book "Kinetics and Mechanism" (1953).

In the spring of 1978 the students were assigned a literature search in the area of quantum mechanics. Then in the spring of 1979 a third set of students were assigned a literature search on topics in the area of chemical kinetics. The students were asked to write a review paper on a minimum of five research articles in the literature on their assigned topic.

There were two main purposes to this activity.

The first purpose was for the student to obtain experience
in searching the literature. The second purpose was for the
student to learn more about concepts in the area assigned by
reviewing literature articles.

An analysis of the student's critiques showed that
the students thought the literature search was worthwhile.
Furthermore, the students preferred to do a literature
search than to perform additional experiments. However,
the students preferred (1) the search involving the develop-
ment of quantum mechanics concepts over (2) the search in-
volving the chemical kinetics reactions. The author
suggests that literature searches on concepts and topics of
research should be continued as an activity to be performed
in the physical chemistry laboratory course. The author
also suggests that this assignment be given at least a
month in advance. In addition, the instructor should insure
that the students begin working on the project as soon as
possible, e.g., the instructor should require the students
to have a list of references by a certain date.

Determination of Transference Numbers
by the Moving Boundary Method

This experiment (Appendix P) was performed by
physical chemistry students at USAFA. It was also performed
by the author at UNC while the physical chemistry students
observed. However, they still performed their own
calculations and each wrote a lab report. The technique
given in this experiment is a modification of different

techniques that were reported in the literature in the early sixties. However, the procedure used in this study has not been reported in the literature.

This experiment enables the student to learn other techniques such as the determination of small volumes by the density method and the use of the technique of graphical integration. It is recommended that the instructor review these techniques with the students. It is also recommended that this experiment be performed after a discussion on irreversible processes in solution in the lecture portion of the course.

The only special apparatus needed is a piece of capillary tubing constricted in 4-6 places and housed in a water jacket. This can be built in a glass blowing laboratory. In fact, if the students are given two laboratory periods to complete this experiment, they can build and calibrate their own piece of moving boundary apparatus.

Writing a Computer Program for the Treatment of a Particle in a One-Dimensional Box

There are few experiments that teach concepts in the area of quantum mechanics. This activity and the next experiment were designed to do just that. In this activity (Appendix Q) the student writes a computer program to simulate a particle in a one-dimensional box. The student gains experience in the use of some mathematical equations used in the area of quantum mechanics. Perhaps for the

first time the student is able to make some abstract concepts more understandable by the use of concrete examples.

The author recommends that other activities like this be included in a physical chemistry laboratory course. It is also recommended that the student be assigned this project at least a month in advance.

The Photoelectric Effect

The last experiment (Appendix R) reviewed in this section, the photoelectric effect, was performed by two physical chemistry students at the USAFA. Similar versions of this experiment have been performed in physics laboratory classes.

For many students the constant, h, in Planck's equation, $E = hv$, is not much more than a "fudge factor." In this experiment the student determines Planck's constant. Thus, maybe for the first time, another abstract concept has more meaning for the student.

When this experiment is being performed, if a monochromator is not available, the instructor may use filters that pass visible light of a narrow bandwidth for a given wavelength. It is recommended that the determination of stopping potentials used to calculate Planck's constant to be performed two to three times for each wavelength. The students can then perform a statistical analysis on their data.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Many curriculum programs have been developed for
use in chemistry, but a review of the literature indicated
that most of those programs had been developed for use in
general chemistry lectures and laboratories. Some programs
have been developed for use in physical chemistry or other
advanced courses. Most of these have been concerned with
modifying how the instruction is presented in lecture,
such as the Keller Plan approach. Few if any programs have
been developed for use in a physical chemistry laboratory
setting. Thus, "A Study to Maximize the Learning
Experiences in the Physical Chemistry Laboratory" was
developed.

This chapter is organized into two sections. The
first section identifies the evidence which supports the
purposes of the study. The second section includes the
author's perceptions, observations and recommendations.

Supporting Evidence

This study was performed with several purposes in
mind. The first purpose was to develop a set of curriculum
materials designed to teach physical chemistry concepts in
the laboratory. As was indicated by the students' scores

on the general laboratory concepts test in chapter III and an analysis of the results of the questionnaires, this goal was achieved.

The second purpose of this study was to revise existing experiments and make them more effective instructional devices. Although there is always room for improvement, the students stated that the modified experiments were more effective than the unmodified one.

The third purpose of this study was to develop new physical chemistry activities. This purpose was achieved, resulting in the following activities being implemented into the physical chemistry laboratory course:

1. An activity on literature searches

2. An activity on computer simulations

3. A modified experiment on transference numbers

4. An experiment to determine Planck's constant

The final purpose of the study was to develop materials designed to increase the higher cognitive skills of the students. This purpose was perhaps the most difficult to measure. From an achievement point of view the ACS test results in this study did not reach a performance considered acceptable by the ACS. However, learning occurred, since the test scores were higher than would statistically be predicted for a random selection of answers. Although learning occurred, the degree to which it occurred is not as great as desired.

In conclusion, the evidence available suggests that:

1. The materials developed do teach physical chemistry concepts in the laboratory

2. New physical chemistry activities were developed

3. The concepts in the area of electrochemistry were <u>not</u> learned to as high a degree as would be desired

Author's Perceptions, Observations and Recommendations

In general a course of study was developed with a format which departed markedly from traditional ways but which is successful enough to justify its continued use. Based on the analysis of the students' questionnaires, the modified materials used in this study were more successful and provided more learning experiences than the unmodified materials.

However, the author in talking with the students felt that the students were more actively involved in the learning process in a laboratory setting. More importantly, the students had a good attitude about learning, and learning is the goal of teaching.

Furthermore, even though this study is not a cure-all for the drawbacks in other educational methods, as Bent said in his article, "You can't win . . . you can improve, and in trying to improve YOU CAN'T LOSE" (1975, p. 448).

Finally, in the author's conclusion, this research has produced a set of modified materials which are more effective in teaching physical chemistry concepts than the unmodified materials were.

The rest of this section gives recommendations for improving the materials developed in this study as well as recommendations for future studies. These recommendations are a result of personal observations as well as students' comments.

Questionnaires

In future studies of this type the questionnaires should have more Likert-method responses, i.e., responses that measure attitude or opinion in a more precise manner. The questionnaire may be analyzed by reporting percentage responses for each individual statement.

Evaluation

An evaluation based on the List of Objectives section should be constructed for each activity to measure each student's learning. These tests as well as test results for all the courses offered by the chemistry department at UNC should be stored for future analysis or comparison. Then if someone wanted to modify some area of instruction, a data base would be available for comparison purposes, which was not the case for this study.

Control Group

Another purpose for storing the test results of the students is that the results could serve as a control group, especially for the smaller courses for which it is not feasible to have a control group. A researcher would then

be able to state whether a modified course of study was an improvement at least with respect to a past group of students.

Replication

The author suggests that the portion of this study which was unsuccessful in proving that physical chemistry concepts could be learned solely in a laboratory setting should be repeated; but in selected areas of physical chemistry containing only a few concepts, e.g., adsorption or surface tension, instead of electrochemistry which has numerous concepts.

Design

Finally, it is recommended that any researcher obtain the necessary approval for the design of his research prior to commencing work on the study.

To Chemical Educators

It is hoped that the materials and results of this study will be useful to chemical educators in achieving the common goal of improving college chemistry instruction.

APPENDIX A

DATA ANALYSIS AND TREATMENT OF ERRORS

NOTE: The material contained in the first activity,
Data Analysis and Treatment of Errors, is an expanded
modification of the material used by Dr. William Koch,
professor of chemistry at the University of Northern
Colorado. In addition, the theory and procedure sections
of experiments 2 - 14 are modifications of unpublished
experiments used by Dr. Koch at UNC, but developed at the
University of Illinois, Urbana. The theory and procedure
sections for experiment # 15 (Appendix N) are modifications
taken from Daniels et al., 1970, p. 113.

APPENDIX A

UNIT 1: DATA ANALYSIS AND TREATMENT OF ERRORS

A. STUDY GUIDE

1. This packet is not meant to be an all encompassing
source for the student, but rather an introduction to it.
For more information on this broad topic the student should
consult one of the references at the start of this UNIT or
one of many other references on this topic.

2. Supply definitions for the KEY WORDS at the beginning
of this UNIT.

3. When using this packet, the student should work each
example problem step by step. Ask your instructor for
help when you need it.

4. It is not necessary to work every problem in this packet,
but you should work out as many as needed to master the
material.

5. You are responsible for meeting the learning objectives
listed for many of the experiments you will perform
this year.

B. OBJECTIVES

1. The student should be able to specify the types of
errors present in a particular experiment as outlined in
UNIT I.

2. The student should be able to define in writing the
terms "precision" and "accuracy" and should be able to
determine the precision and accuracy of experimental
measurements.

3. The student should be able to write the final result of
a measurement or calculation with the correct number of
significant figures.

4. The student should be able to calculate the average
error, standard deviation, and probable error for the
result of an experimentally determined value.

5. The student should be able to calculate the maximum
error associated with a particular result.

6. The student should be able to reject specific experimental values from a number of determined values when their validity is not sufficient to be retained.

7. In all laboratory reports the student should be able to graph his data and label his graph.

8. The student should be able to treat graphical data numerically in at least one of the three methods outlined, preferably the method of least squares.

C. KEY WORDS (Supply equations where possible.)

Absolute deviation from the mean, d

Arithmetic mean, $\bar{x}$

Average error or deviation, a

Function, any, u

Intercept, b

Maximum error of function, Δu

Number of measurements, n

Probable error, σ_p

Range in statistics, R

Slope, m

Standard deviation, σ

Student deviation, σ_s

Variance, σ^2

D. REFERENCES AND SUPPLEMENTAL READING LIST

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3. Crockford, H. D., and J. W. Nowell, "Laboratory Manual of Physical Chemistry," John Wiley, New York, 1976.

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5. Klotz, I. M., "Chemical Thermodynamics," Benjamin, New York, 1964.

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11. Wilson, J. M., et al., "Experiments in Physical Chemistry," Pergamon Press, New York, 1968.

12. Worthing, A. G., and J. Geffner, "Treatment of Experimental Data," John Wiley, New York, 1943.

13. Young H. D., "Statistical Treatment of Experimental Data," McGraw-Hill, New York, 1962.

I. INTRODUCTION (Koch 1976)

In the main, these courses have not been designed
to acquaint you with experimental techniques employed
almost daily by persons active in research, development, or
service work of which physicochemical investigations are a
part. However, they should teach you many of the fundamental
concepts in physical chemistry. They have been designed to
acquaint you with a certain point of view, the critical
point of view. Thus, it is hoped that when you have
finished the prescribed work, you will have acquired some
experience in judging the care and precision with which you
can perform laboratory measurements under a variety of
conditions, in estimating the probable errors in the
calculated final results of your own experimental efforts,
and in interpreting and evaluating conclusions based on
those final results. This handout should not be thought of
as a single all encompassing source, but rather as an
introduction. The student is invited to make use of one or
more of the supplemental readings for a more thorough under-
standing of this complex subject.

A. KINDS OF ERRORS

Physical measurements are subject to three types of
errors: (a) mistakes or blunders; (b) determinate or
systematic errors; and (c) indeterminate or random errors.
Those of the first type include mistakes in recording data
and gross mistakes or blunders in reading scales, such as
recording a 9 when it should be a 5 or reading a scale
backward. The second type of error is that kind which
affects all measurements alike. They may be instrumental;
operative, i.e., use of instruments; or personal. An
example of these would be the consistent over or under
estimation of fractions of scale divisions by the observer,
e.g., reading a graduated cylinder. Another example would
be the faulty apparatus which causes a consistent error in
one direction, e.g., a meter stick which is off. The first
two types of errors can be minimized by taking care in
making observations, verifying that the equipment is
operating correctly, and by compensating for systematic
errors. The third type of error, a random error, cannot be
determined for a specific reading and is always present to
a greater or lesser degree in any physical measurement.

B. PRECISION AND ACCURACY (Crockford and Nowell 1976)

Prior to further discussion of errors we need to
look at measurements themselves. When is a measured value
accurate? The accuracy pertains to how close the measured
result compares to the true value, or in other words the

correctness of the result. However, high accuracy is improbable without good precision. <u>Precision</u> is a measure of how reproducible the result is, or in other words the number of significant figures in its value. When the precision of a number is to be reported the error associated with the number is also reported.

<u>EXAMPLE 1-1</u>: In reporting a weighing the value might be 33.3330 ± 0.0002 g. This indicates that the actual value lies between 33.3328 and 33.3332 g. Thus the ± 0.0002 g is a measurement of the precision of the reading.

C. SIGNIFICANT FIGURES AND RULES (Oelke 1969)

All the known (or certain) digits in a measurement of a quantity plus the first estimated or doubtful digit are called significant figures. In reporting a measured value we will use the following rules:

1) No more than the final digit may be uncertain; other uncertain digits should be dropped. This is especially true when reading values from a calculator since they usually display more than you are allowed.

<u>EXAMPLE 1-2</u>: The number 33.33 ± 0.3 g should be reported as 33.3 ± 0.3 g.

2) The leftmost nonzero digit is referred to as the most significant digit.

<u>EXAMPLE 1-3</u>: For the value 123.34 ml, the "1" is the most significant digit.

3) It should be quite apparent that all digits actually obtained by measurement are significant.

4) The significance of a zero in calculations involving measured numbers is truly an adventure in frustration. Is zero a measured digit, or does it serve merely to locate the decimal point? Zero is significant only if it is a measured or estimated value. It is not significant when it is used to locate the decimal point.

5) Trailing zeros in a whole number, such as 5280 ft, create a more difficult problem. Unless we know something about the means by which the measurement was obtained or about the intent of the person who recorded this piece of data, we do not know whether 5280 ft contains three or four significant figures. In this course, we will use the rule that all zeroes in whole numbers will be assumed to be significant figures unless you have reason to know otherwise.

6) If any zeroes in a whole number are not significant, you must express the number in exponential form.

7) If there is a decimal point, the rightmost digit is the least significant one, even if it is a zero.

EXAMPLE 1-4: The "0" in 21.640 g is the least significant digit.

8) All digits between the least and most significant digits are counted as significant digits.

EXAMPLE 1-5: For the value 30.0608 g there are a total of six significant digits.

9) In addition and subtraction, retain only as many decimal places as are present in the component with the least number of decimal places. This presupposes that all numbers have decimal points or that the decimal points are correctly assumed.

EXAMPLE 1-6: In adding 9.0 + 12.90 + 1.290 = 23.190, the answer 23.190 must be rounded off to 23.2. It should be noted that the least precise number contains two significant figures, but that the the answer contains three. This will happen often in addition and subtraction and is correct.

10) In multiplication and division, the final result should have the same number of significant figures as the measurement with the least number of significant figures.

EXAMPLE 1-7: In multiplying 0.76 x 1.24 x 2.449 we obtain 2.3079376 when we retain all the digits. The least certain measurement is 0.76 which contains only two significant figures. Therefore, the final result should be reported as 2.3.

PROBLEM SET 1-1: Perform the operations indicated applying the rules of significant figures:

1. 308.7812 + 0.00034 + 10.31 =

2. (364.32)(6.31) =

3. 76.512/1.432 =

4. $\dfrac{31.9988 \times 0.08205 \times 273.12}{1.000 \times 22.41383}$ =

NOTE: Discrete numbers may be considered to have an infinite number of significant digits.

II. STATISTICAL METHODS

It must be recognized that all experimentally determined values have an inherent uncertainty due to the unavoidable errors associated with all measurements. However, it is possible to calculate a "best value" (Crockford and Nowell 1976) from a set of determined values. A range of uncertainty is usually assigned to this most probable value. For example, if the most probable value for a velocity is V_p, the true value, V_t, should lie within the range $V_p \pm R$, where R represents the range of uncertainty of the most probable value. As another example, consider measuring the length of an object. The true value, l_t, should be $l_p \pm R$.

In physical chemistry experiments, two general types of error analysis are required. The first involves a set of measurements from which nothing is calculated, for example, the counting rate of a radioactive sample. If the counting rate of a radioactive sample is determined several times, each measurement will probably yield a somewhat different value, e.g. 1111, 1122, 1100, 1115, 1108, etc. The problem then is to determine the best value for the counting rate and to assign a range of uncertainty to this best value.

The second type of analysis involves a derived result in which several measurements, each with a particular uncertainty are combined to yield a final result. The question to be answered is how the uncertainties of the various measurements should be combined. A common example is the determination of the mass of an object by the difference between the weight of the object and its tare, and the tare alone. A tare is the weight of the container used to hold the object. This type of analysis will be discussed under propagation of errors.

We start our statistical treatment with the easiest calculation we can make, that of the <u>arithmetic mean</u>, $\bar{X}$. The mean is often referred to as simply an average. This is exemplified as follows:

EXAMPLE 1-8: If we have a set of measurements for the molecular weight of some substance say 78, 79, 80, 77, 81, 78, and 80, the arithmetic mean would simply be the sum of the numbers symbolized by the Greek letter sigma, Σ, divided by the total number of measurements in the set, or in algebraic language

$$\bar{x} = \frac{\Sigma x}{n} \tag{1-1}$$

where the limits of summation are omitted and the summation is understood to extend over all available values of x. In this example

$$\bar{x} = \frac{553}{7} = 79. \quad \text{(How many significant figures, SF?)}$$

ANS: Two - Why? Seven is a discrete number.

A. AVERAGE ERROR   (Crockford and Nowell 1976)

Once we obtain a number of measurements we are concerned with the error associated with those measurements. The average error, a, or mean deviation as it is sometimes called is a measure of the sum of the absolute deviations from the mean, d, divided by the total number of measurements. Algebraically it is

$$a = \frac{\Sigma |x - \bar{x}|}{n} = \frac{\Sigma d}{n} . \qquad (1\text{-}2)$$

EXAMPLE 1-9: As a sample, we will calculate the average error associated with Example 1-9.

x	78	79	80	77	81	78	80
$\bar{x}$	79	79	79	79	79	79	79
d	1	0	1	2	2	1	1

Therefore, $a = \frac{\Sigma d}{n} = \frac{8}{7} = 1.14.....\approx 1.$

We would then express the molecular weight of our substance as 79 ± 1.

PROBLEM 1-2: For the following set of measurements calculate the arithmetic mean and the average error: 15, 17, 14, 20, 15, and 19.

B. STANDARD DEVIATION   (Daniels et al., 1970)

Some of the deviations about the mean are positive; others are negative; while the sum of the deviations is zero. One method for dealing with the presence of negative signs is to use the absolute deviations, as in the calculation of the mean deviation. Statistically this procedure has little to recommend it. A preferable procedure is to square the deviations about the mean, sum these squares, and use this sum of squares in the definition of a measure of variance, σ^2. The standard deviation, σ, is then

$$\sigma = \sqrt{\frac{\Sigma d^2}{n}} \qquad (1\text{-}3)$$

Student Deviation: A reliable statistical analysis using Equation 1-3 requires many measurements. Most physical chemistry experiments allow only a limited number of determinations. In such cases, an uncertainty known as the "Student Deviation", σ_s, is often preferable. Algebraically it is

$$\sigma_s = \pm\sqrt{\frac{\Sigma d^2}{n-1}} \qquad (1\text{-}4)$$

Equation 1-4 is the same as 1-3 except that we

divide by n-1 rather than by n. The reason is a statistical one. Division by n-1 rather than n provides a sample standard deviation that is a better estimator of the standard deviation of the population from which the sample was drawn.

C.   PROBABLE ERROR   (Daniels et al., 1970)

The probable error is determined in such a way such that half of the deviations from the arithmetical mean (d) are larger and half are smaller than the probable error. Therefore, the error of an additional measurement has a 50-50 chance of being smaller than the probable error. The probable error of an individual measurement is defined as

$$\sigma_p = 0.6745 \sqrt{\frac{\Sigma d^2}{n-1}} \qquad\qquad (1-5)$$

For most purposes we will be interested in using the student standard deviation. Therefore, in most student calculations of errors Equation 1-4 should be used.

PROBLEM 1-3: Given the following test scores for two groups of people taking an exam, one taking an experimental drug during the test while another a control group is given an inert pill. Compare the means, average error, standard deviation, and probable error for the two groups.

Experimental	5	7	17	31	45	47	68	85	96	99
Control	29	36	37	42	49	58	62	63	69	70

D.   REJECTION OF DATA   (Salzberg et al., 1969, p. 16)

When one makes a limited number of experimental measurements of the same quantity, it is not legitimate to reject a specific value regardless of how much it may vary from the other values unless there is some known reason which caused an error in the value. However, when one has a group of four or more experimentally determined measurements and there is one value that doesn't seem to fit, the following is one of the procedures that may be employed to determine whether or not a value can be discarded when the reason why it is in disagreement is not known.
(a) Calculate the mean, $\overline{X}$, omitting the doubtful value.
(b) Calculate the average deviation from this mean, a.
(c) Calculate the deviation from the mean of the doubtful value.

If the deviation from the mean of the doubtful value is equal to or greater than four times the average deviation, $\geq 4a$, the doubtful value may be discarded. A minimum of 4 observations must be made before the test can be applied.

According to probability theory, 99.3% of all observations have errors equal to or less than 4 times the average deviation, $\leq 4a$.

PROBLEM 1-4: A set of six experimental runs on a sample of iron ore yielded the following percentages of Fe_2O_3, 51.25, 51.20, 51.27, 51.30, 51.22, and 51.60. On the above basis which if any value can be rejected?

E. PROPAGATION OF ERRORS OF DERIVED RESULTS (Shoemaker and Garland 1962 p. 31)

The second type of error analysis which must be applied to physical chemistry measurements involves the assignment of an uncertainty to a calculated result obtained by application of a formula involving several different values, all with associated uncertainties. For example, in molecular weight determination, by the method of Victor Meyer or Dumas, the formula $M = gRT/PV$ is applied. The experimental quantities g, T, P, and V all have associated uncertainties and the resulting uncertainty in M must be determined. M is often called a derived quantity. The error of all derived quantities will depend upon the errors of the associated experimental values.

Two methods are applicable in assigning errors to derived quantities. The first is applicable if a large number of determinations is made in which case the preceding statistical formulas may be applied to determine the magnitude of the errors associated with each measured quantity. These errors can then be combined to yield a reliable estimate of the error of the derived result.

However, as you will soon see it is generally not possible to repeat measurements in the physical chemistry laboratory more than a couple of times. Thus, you are not justified in using the statistical formulas to assign uncertainties. This brings us to the second method of assigning errors, that of estimating uncertainties. For instance, you should be able to estimate maximum errors in directly measured quantities such as weights, volumes, pressures, and temperatures. Then you will use these estimates to calculate the uncertainty for some result, e.g., molecular weight, which can not be measured directly.

The estimate of the error may be the actual manufacturer's designated uncertainty or it may be unknown. In the latter case, the student must assign an uncertainty based on how precisely he feels he can read the measuring device. For example, a thermometer graduated in tenths of a degree Celsius may be read to at least the nearest $\pm 0.1°C$, or a calibrated burette may be read with a lens to ± 0.02 ml.

Maximum Error of a Derived Result: Most experimental results are obtained by calculating some function of directly measured quantities. Let u be the derived result, and let this derived result be a function of x, y, and z. For u = f(x,y,z), the total differential of u is given by

$$du = \left(\frac{\partial u}{\partial x}\right)_{y,z} dx + \left(\frac{\partial u}{\partial y}\right)_{x,z} dy + \left(\frac{\partial u}{\partial z}\right)_{y,z} dz \qquad (1-6)$$

The partial derivatives are derived from the relation by means of which u itself is calculated. This will be evident in Example 1-10. Equation 1-6 gives the change in the derived function u when infinitesimal changes in the quantities x, y, and z occur, i.e., dx, dy, and dz. The change in u, du, may also be looked upon as the variation or error associated with infinitesimal variations or errors in x, y, and z. For small but finite variations in x, y, and z the differentials may be replaced by finite increments.

$$\Delta u = \left|\left(\frac{\partial u}{\partial x}\right)_{y,z}\right| \Delta x + \left|\left(\frac{\partial u}{\partial y}\right)_{x,z}\right| \Delta y + \left|\left(\frac{\partial u}{\partial z}\right)_{x,y}\right| \Delta z \qquad (1-7)$$

NOTE: In calculating the maximum error, Δu, the signs of all quantities are chosen such that all terms add together in a positive sense. Thus we are really adding the absolute value of each term together. It is also important to note that if the uncertainty of the experimentally measured quantities are not properly estimated, the maximum error calculation loses its significance.

It should also be noted that $\Delta x/x$ represents the relative error in x, and the relative error times 100 gives the percent error. First a simple example using only the variables x and z.

EXAMPLE 1-10: If $u = 4.35x^3 - 6.55x^2 z + 1.22xz^2 + z^3$, find the error in u if $x = 4.23 \pm 0.07$ and $z = 1.65 \pm 0.02$. Give both the absolute and relative error.

$$\left(\frac{\partial u}{\partial x}\right) = 3(4.35)x^2 - 2(6.55)xz + 1.22z^2$$

$$\left(\frac{\partial u}{\partial z}\right) = -6.55 x^2 + 2.44 xz + 3z^2$$

$$\Delta u = \left(\frac{\partial u}{\partial x}\right)\Delta x + \left(\frac{\partial u}{\partial z}\right)\Delta z = 145.39(0.07) + \left|-92.00\right|(0.02)$$

$$\Delta u = 10.18 \qquad 1.84 = \underline{12.02 \text{ (Absolute value)}}$$

$$u = 4.35(4.23)^2 - 6.55(4.23)^2(1.65) + 1.22(4.23)(1.65)^2 + (1.65)^3$$

$$u = 154.4$$

$$\text{Relative error} = \frac{\Delta u}{u} = \frac{12.02}{154.4} = 0.0778 = \underline{7.78\% \quad (3SF)}$$

PROBLEM 1-5: If $u = y^2 v^3 / (w^{\frac{1}{2}} x^{\frac{1}{2}} z^{\frac{1}{4}})$, derive an equation for the relative error in u for given errors in all the other variables. If the following per cent errors are known, find the per cent error in u: y - 1.3%, v - 0.6%, w - 2.2%, x - 0.33%, and z - 1.02%.

EXAMPLE 1-11: Application of equation 1-7 can be made to a gaseous molecular weight determination like the Dumas method. The Dumas method is used to determine the molecular weight of a volatile substance. Assuming the uncertainties in the weight, temperature, pressure, and volume are known, we have

$$M = \frac{gRT}{PV} \quad \text{and}$$

$$\Delta M = \left| \frac{\partial M}{\partial T} \right|_{g,P,V} \Delta T + \left| \frac{\partial M}{\partial P} \right|_{g,T,V} \Delta P + \left| \frac{\partial M}{\partial g} \right|_{P,T,V} \Delta g + \left| \frac{\partial M}{\partial V} \right|_{g,P,T} \Delta V$$

The first of the partials for the derived quantity M is:

$\left(\frac{\partial M}{\partial T} \right)_{g,P,V} = \frac{gR}{PV}$, and since $\frac{gR}{PV} = \frac{M}{T}$, then $\left(\frac{\partial M}{\partial T} \right)_{g,P,V} = \frac{M}{T}$.

The other partials are treated in the same manner.

$$\left(\frac{\partial M}{\partial P} \right)_{g,T,V} = -\frac{gRT}{P^2 V} = -\frac{M}{P}$$

$$\left(\frac{\partial M}{\partial g} \right)_{P,T,V} = \frac{RT}{PV} = \frac{M}{g}$$

$$\left(\frac{\partial M}{\partial V} \right)_{g,P,T} = -\frac{gRT}{PV^2} = -\frac{M}{V}$$

Each partial gives the rate of change of M with the variation of a variable and consequently when multiplied by the uncertainty of the variable, e.g., ΔT, the error of the derived quantity is obtained.

$$\Delta M = \left| \left(\frac{M}{T} \right) \right| \Delta T + \left| \left(-\frac{M}{P} \right) \right| \Delta P + \left| \left(\frac{M}{g} \right) \right| \Delta g + \left| \left(-\frac{M}{V} \right) \right| \Delta V \qquad (1-8)$$

Now we will apply the above to some data obtained in a molecular weight determination, where the values are as follows:

Quantity Measured	Uncertainty
g = 0.1273g	± 0.0002 g
T = 298 K	± 1.0 K
P = 566 mm Hg	± 1.0 mm Hg
V = 57.1 cc	± 0.1 cc

Given that R equals 82.07 mL-atm/mole-K and assuming that the uncertainty in R is insignificant compared to the measured quantities we obtain a value for M of

$$M = \frac{gRT}{PV} = \frac{(0.1273)(82.07)(293)}{(566/760)(57.1)} = \underline{73.2 \text{ g/mole}}$$

Now solving for each term in Equation 1-8, the following is obtained:

$$\left(\frac{\partial M}{\partial T}\right)_{g,P,V} = \frac{M}{T} = \frac{73.2}{298} = 0.245$$

$$\left(\frac{\partial M}{\partial P}\right)_{g,T,V} = -\frac{M}{P} = -\frac{73.2}{566} = -0.129$$

$$\left(\frac{\partial M}{\partial g}\right)_{P,T,V} = \frac{M}{g} = \frac{73.2}{.1273} = 574$$

$$\left(\frac{\partial M}{\partial V}\right)_{g,P,T} = -\frac{M}{V} = -\frac{73.2}{57.1} = -1.28$$

Inserting the above value into Equation 1-8 we obtain the desired results.

$$\Delta M = \left|\left(\frac{M}{T}\right)\right|\Delta T + \left|\left(\frac{-M}{P}\right)\right|\Delta P + \left|\left(\frac{M}{g}\right)\right|\Delta g + \left|\left(\frac{-M}{V}\right)\right|\Delta V$$

$$= (.245)(1.0) + (.129)(1.0) + (574)(.0002) + (1.28)(0.1)$$

$$= \quad 0.245 \quad + \quad .129 \quad + \quad .115 \quad + \quad .128$$

$$= \quad \underline{0.617} \text{ g/mole}$$

and thus

$$M = 73.2 \pm 0.6 \text{ g/mole}$$

The method also distinctly defines the measurement which contributes most to the uncertainty, in this case the temperatue uncertainty.

PROBLEM 1-6: The molar refraction for a fluid is defined by the relation: (Daniels et al., 1970, p. 436)

$$\mathcal{R} = \frac{n^2-1}{n^2+2} \frac{M}{\rho}$$

where M = molecular weight, n = refractive index, and ρ = density of fluid.

At 25°C and 1 atmosphere pressure the following results are specified for liquid benzene, for which the molecular weight may be assumed a constant with a value of 78.114 g/mole. Solve for the molar refraction and its maximum error, where

ρ = 0.8737 ± 0.0002 g/ml and
n = 1.4979 ± 0.0003 (unitless)
....

A slightly different form for equation 1-7 is used for derived quantities involving variables raised to some power.

$$u = x^{\pm a} \cdot y^{\pm b} \cdot z^{\pm c}$$

In this case before applying Equation 1-6 we take the logarithm of both sides.

$$\ln u = \pm a \ln x \pm b \ln y \pm c \ln z$$

Now we can take the derivative of both sides directly since the variables are separated. Remembering that $d(\ln x) = dx/x$, we have

$$\frac{du}{u} = \pm a \frac{dx}{x} \pm b \frac{dy}{y} \pm c \frac{dz}{z} \qquad (1-9)$$

As before we again replace the differentials with finite increments.

$$\left|\frac{\Delta M}{M}\right| = |a|\left|\frac{\Delta x}{x}\right| + |b|\left|\frac{\Delta y}{y}\right| + |c|\left|\frac{\Delta z}{z}\right| \qquad (1-10)$$

Equation 1-10 represents the fractional error of the derived quantity. The terms on the right such as $\Delta x/x$ represent the relative error of the variables. Equations 1-9 and 1-10 apply for all exponents including ± 1. Thus, this procedure is a more general one and may be used in calculation errors involving the multiplication and/or division of uncertainties including cases such as the molecular weight example considered earlier.

Composite Quantities: Many derived results require the use of values obtained by the combination of two or more independent measurements. For example, most sample weights

are obtained by substracting a container weight from a container plus the weight of the sample. The error of the composite quantity is not usually the same as that of the independent measurements.

EXAMPLE 1-12: In the simple case of two variables with their associated uncertainties being added together, we may use Equation 1-7.

$$u = x + y$$

$$\Delta u = (\frac{\partial u}{\partial x})\Delta x + (\frac{\partial u}{\partial y})\Delta y$$

but $(\frac{\partial u}{\partial x}) = \frac{dx}{dx} = 1$

and $(\frac{\partial u}{\partial y}) = \frac{dy}{dy} = 1$

giving $\Delta u = \Delta x + \Delta y$

Thus adding the two terms yields

$$u \pm \Delta u = (x + y) \pm \left| \Delta x + \Delta y \right| \qquad (1-11)$$

Given below are some simple results which may be used in maximum error calculations (Daniels et al., 1970, p. 437).

For subtraction, i.e., $u = x - y$

$$u \pm \Delta u = (x-y) \pm \left| \Delta x + \Delta y \right| \qquad (1-12)$$

For multiplication, i.e., $u = (x)(y)$

$$u \pm \Delta u = (xy) \pm \left| y\Delta x + x\Delta y \right| \qquad (1-13)$$

For division, i.e., $u = x/y$

$$u \pm \Delta u = \frac{x}{y} \pm \left| \frac{\Delta x}{y} + \frac{x\Delta y}{y^2} \right| \qquad (1-14)$$

PROBLEM 1-7: Using Example 1-12 as a guide, show how Equations 1-12 and 1-13 were determined.

EXAMPLE 1-13: Complete analysis of a Dumas method molecular weight determination yields the following data:

Weight of empty bulb $W_1 = 57.1423 \pm 0.002$ g

Weight of bulb + water $W_2 = 278.8 \pm 0.2$ g

Density of water $\rho_w = 0.998 \pm 0.001$ g/mL

Weight of bulb + sample	W_3	$= 57.7432 \pm 0.0002$ g
Temperature	T	$= 365 \pm 1$ K
Atm. pressure	P	$= 567 \pm 1$ mm
Density of air	ρ_a	$= 0.00120 \pm 0.00001$ g/mL

By using the Dumas method, molecular weights of solids or liquids that vaporize without decomposition may be calculated from the densities of their vapors. Deviations from the true molecular weight are greater for such substances than for ideal gases because of the nonideality of the vapors. In this method the molecular weight is determined by the use of the rearranged form of the ideal gas law equation,

$$M = \frac{gRT}{PV}.$$

It should be noted from the data given above that two of the quantities (g and V) are composite quantities obtained by the combination of two or more measurements. The maximum errors of the composite quantities are calculated first and then the error of the final results are determined. For the weight of the gas we have

$$g = w_3 - (w_1 - (\frac{w_2 - w_1}{\rho_w})\rho_a)$$

$$= 57.7432 \pm .002 - (57.1423 \pm .0002) - (\frac{278.8 \pm .2 - 57.1423 \pm .002}{0.998 \pm 0.001}) \text{ times}$$
$$(.00120 \pm .00001)$$

$$= 0.6009 \pm 0.0004 + \frac{221.7 \pm 0.2}{0.998 \pm .001}(.00120 \pm .00001)$$

$$= 0.6009 \pm 0.0004 + 221.7 \pm 0.2(0.00120 \pm 0.00001)$$

$$= 0.6009 \pm 0.0004 + 0.2660 \pm 0.00246$$

$$g = \underline{0.8669 \pm 0.0029} \text{ g}$$

$$V = \frac{w_2 - w_1}{\rho_w}$$

$$= \frac{278.8 \pm 0.2 - 57.1423 \pm 0.0002}{0.998 \pm 0.001}$$

$$V = \frac{221.7 \pm 0.2}{0.998 \pm 0.001} = \underline{222.1 \pm 0.4} \text{ mL}$$

M is then calculated in the same manner as Example 1-11.

PROBLEM 1-8: This problem involves determining the initial
pressure of a gas, the final pressure after it has been
cooled, and the associated pressure change. The errors in
an experiment of this type result from the uncertainties
associated with reading a rather crude manometer. The
pressure is obtained by determining the difference in the
heights of the mercury in the two arms of the manometer.
Let R equal the reading in mm of mercury in the right arm of
the manometer. Let L equal the reading of the left arm of
the manometer. Let H equal the difference in the height
of mercury in both arms of the manometer.

Initial Readings	Final Readings
$R_o = 53.0 \pm 0.5$ mm	$R = 43.0 \pm 0.5$ mm
$L_o = 17.0 \pm 0.5$ mm	$L = 27.0 \pm 0.5$ mm

Find the pressure in mm of mercury and the maximum error
associated with that result. Show all your work.
. . . .
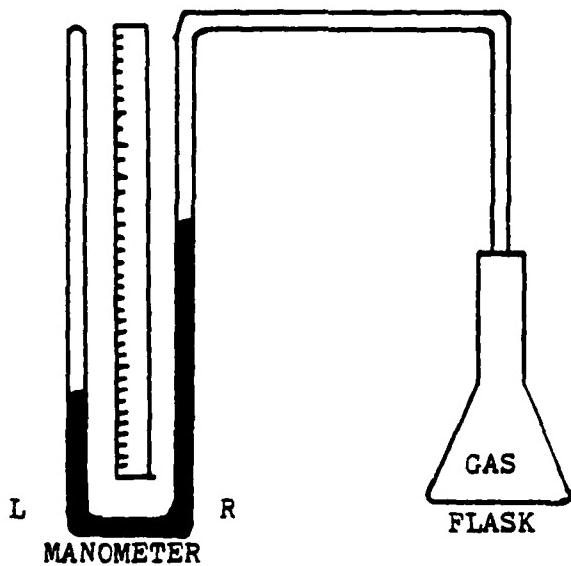
FIGURE 1-1: Manometer for Problem 1-8

III. METHODS OF ANALYSIS

A. REPRESENTATION OF DATA BY GRAPHS   (Koch 1976)

       Graphs have many advantages which favor their use in representing data. Cne of the most important of these advantages is that a graph may reveal maxima, minima, inflection points, or other significant features in data which might be overlooked in a tabular or formula representation. These features are illustrated on Figure 1-2. Furthermore, direct differentiation may be performed by drawing tangents to a curve, or by other techniques, and integration may be accomplished by determining the area under a curve. In many cases these operations would otherwise be tedious or impossible.

       The steps to be followed in preparing a satisfactory graph have been extensively treated and illustrated with numerous examples by Worthing and Geffner ("Treatment of Experimental Data," John Wiley and Sons, Inc., New York, 1943). We shall summarize here only some of the more important points. As an example see the graph in Figure 1-3.

I. <u>Choosing the graph paper.</u> Crdinary rectangular coordinate paper such as used in Figures 1-2 and 1-3 is satisfactory for most purposes. Semilogarithmic paper as shown in Figure 1-4 is convenient when one of the coordinates is to be the logarithm of an observed variable, e.g., Vapor Pressure-Dynamic Method: Experiment 4 (Crockford and Nowell 1976). If both coordinates are to be logarithms of variables, log-log paper, e.g., Figure 1-5, may be used. Determination of the slope of a straight line plot is easiest, however, when rectangular coordinate paper is employed. Another special-purpose paper which has triangular coordinates, shown Figure 1-6, is used in phase diagrams, e.g., Solubility Diagram, Three-Component System: Experiment 19 (Crockford and Nowell 1976).

II. <u>Choosing the coordinate scales.</u> The following rules are listed by Worthing and Geffner. They are not altogether inflexible and common sense should prevail.

1. The scale for the independent variable should be measured along the X-axis (abscissa). The method employed in the experiment usually determines the independent variable. For example, if you are measuring the vapor pressure of a gas at various temperatures, the vapor pressure is dependent on the temperature. This makes the pressure the dependent variable and the temperature the independent variable.
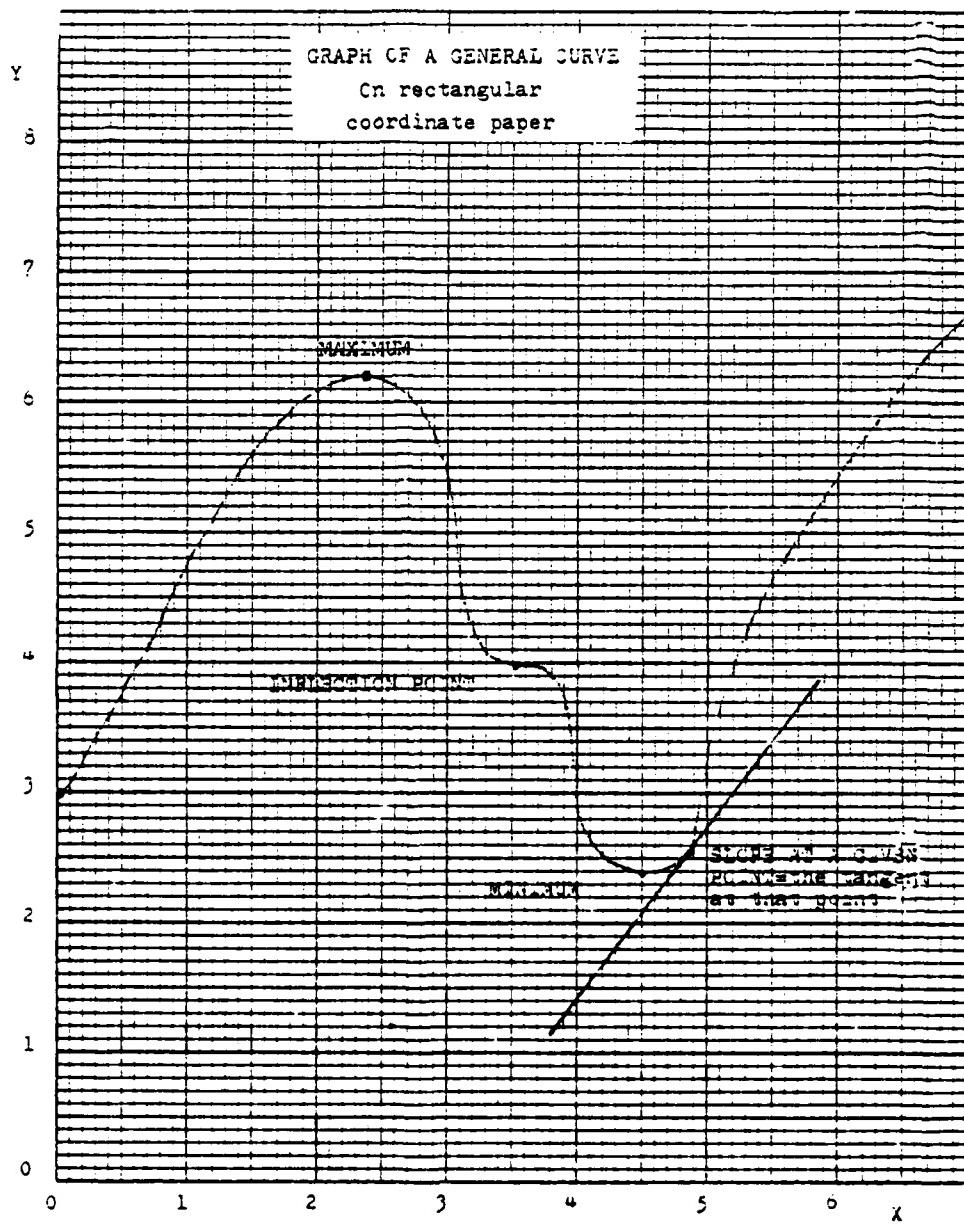
FIGURE 1-2 Significant features revealed by graphs.

FIGURE 1-3. Graphical example using rectangular coordinate paper.
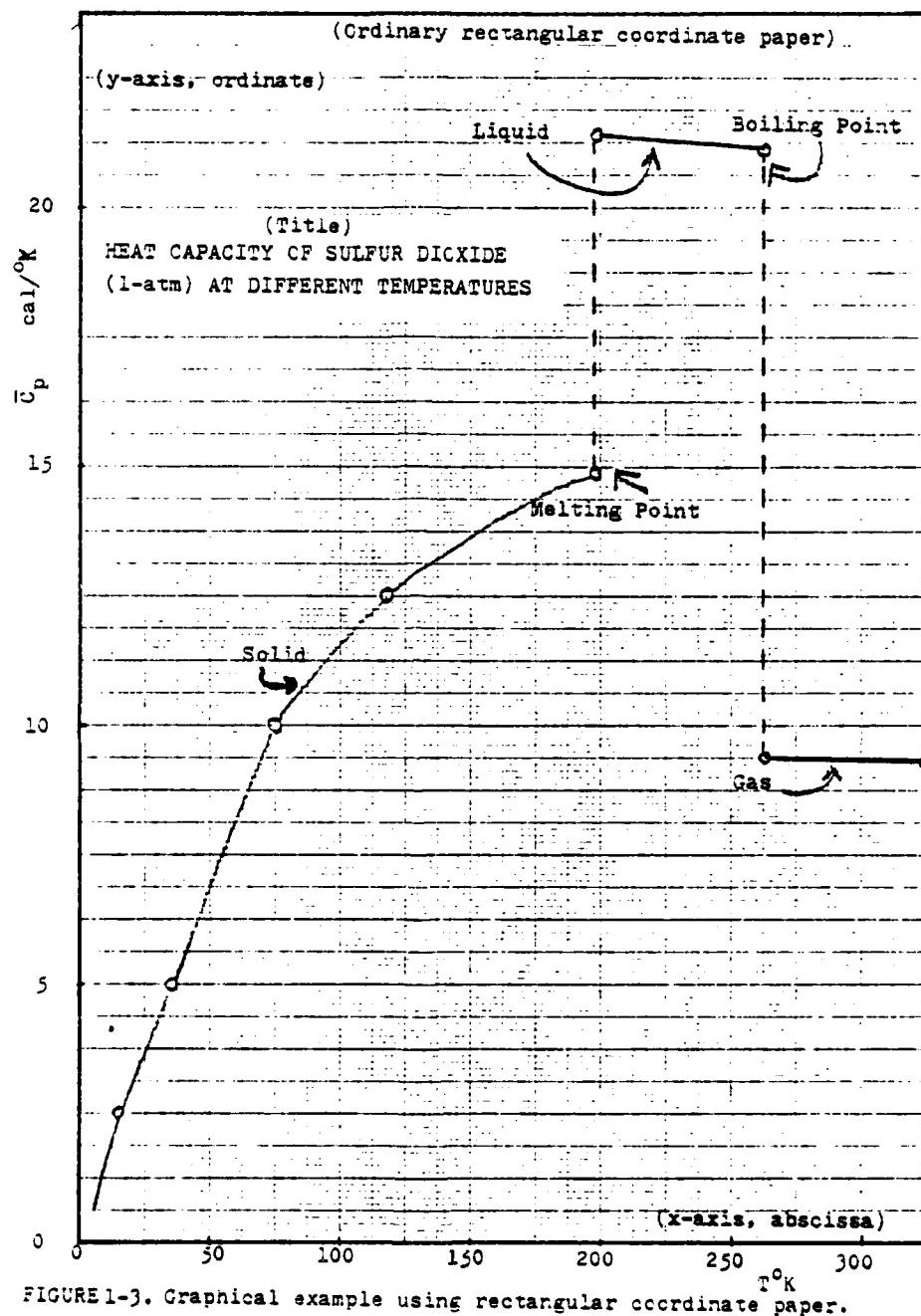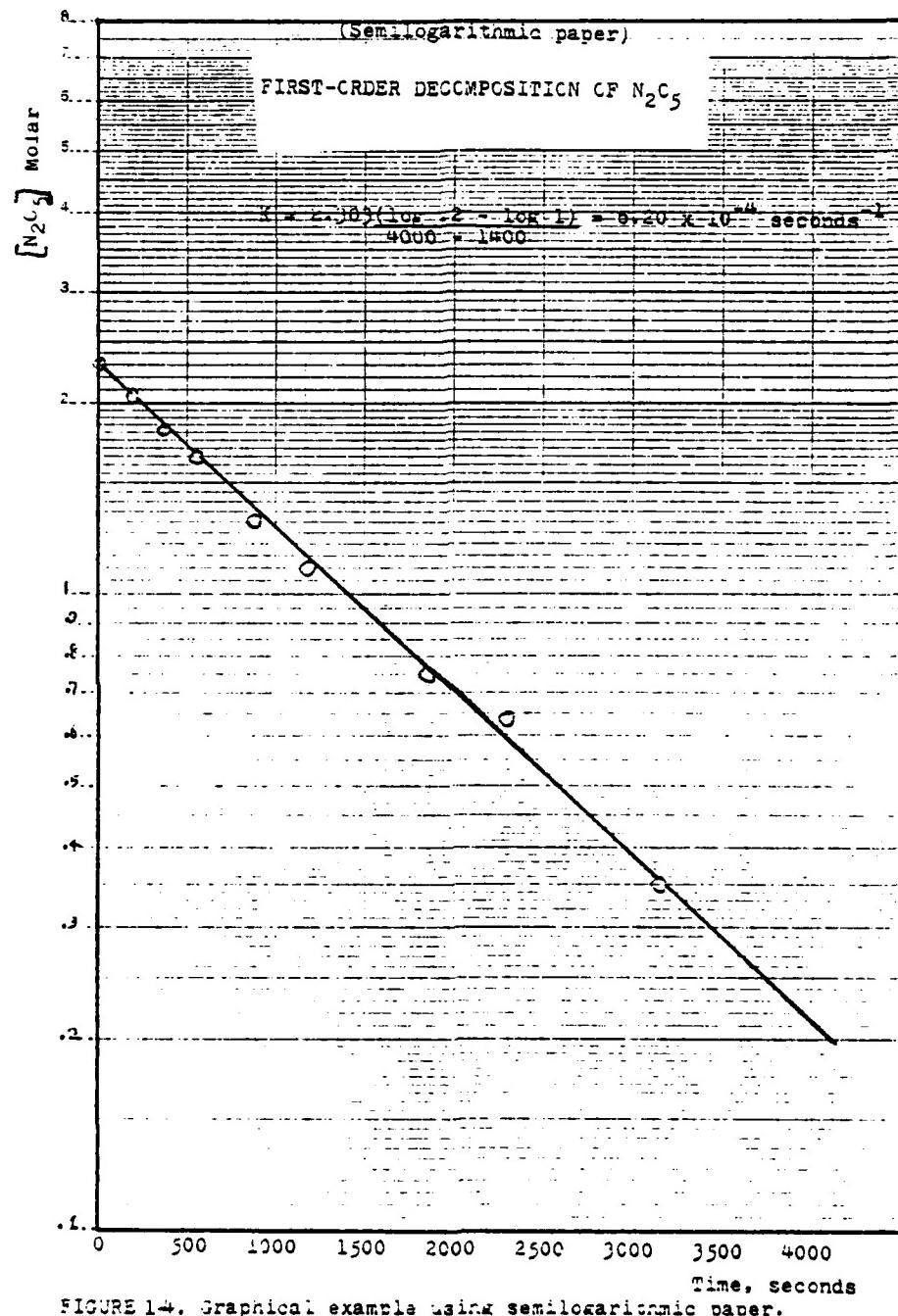
FIGURE 14. Graphical example using semilogarithmic paper.
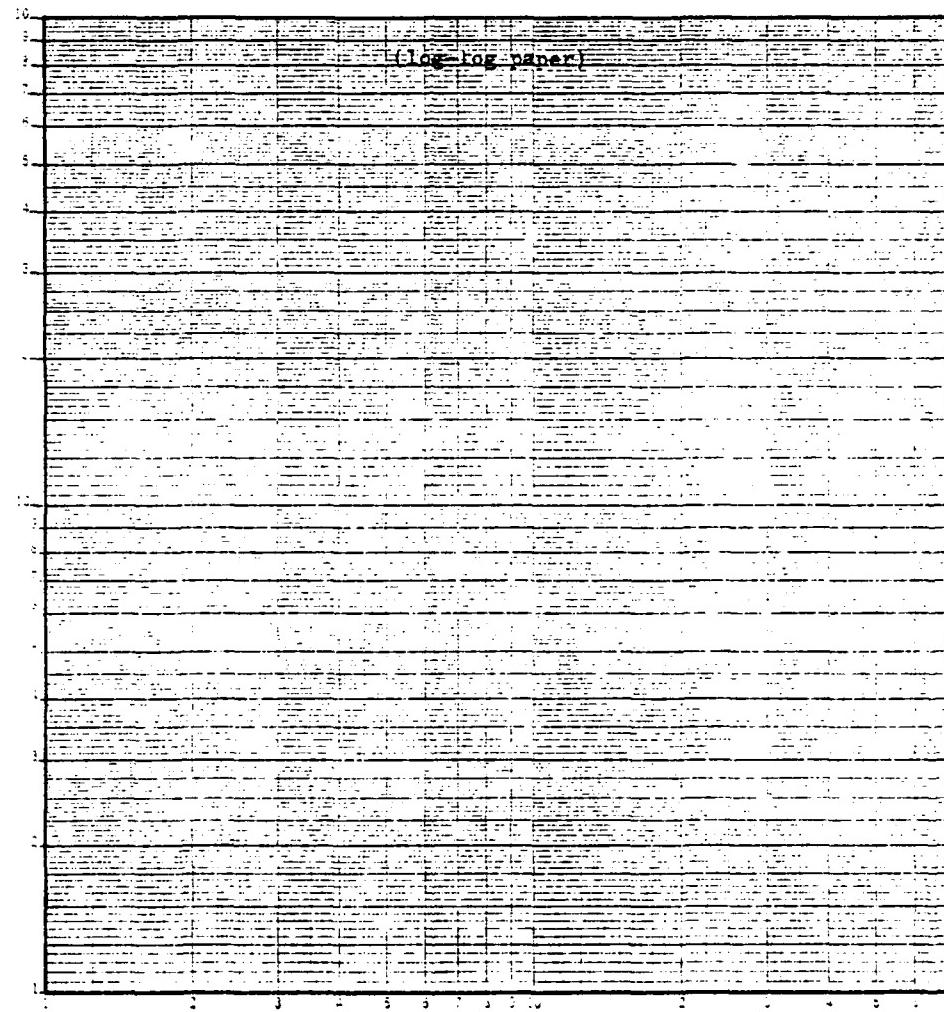
(log-log paper)

FIGURE 1-5. Sample of log-log paper.

85

SOLUBILITY DIAGRAM
THREE-COMPONENT SYSTEM
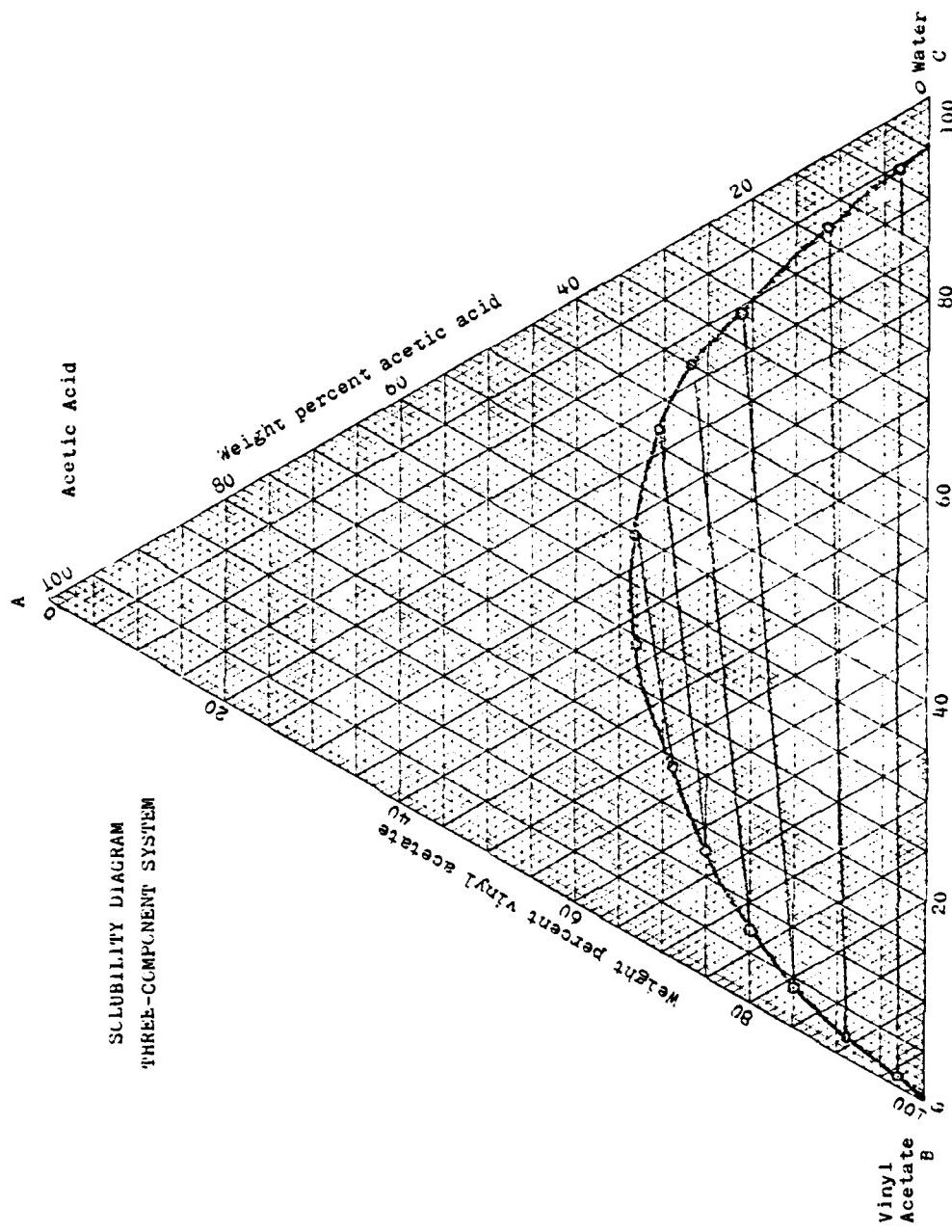
FIGURE 1-6. Graphical example using three component paper

2. The scales should be so chosen that the coordinates of any point on the plot may be determined quickly and easily. For example, in using rectangular coordinate paper such as given in Figure 1-3, there are ten minor divisions between every major division. Assigning a scale which increases by three units for every major division would cause each minor division to increase by three tenths. On this scale numbers such as 1.0 or 2.2 would be difficult to locate.

3. The scales should be established so that the resultant curve is as large as the sheet can conveniently permit, provided that the uncertainties or measurement do not correspond to more than one or two of the smallest divisions. It should be noted that the larger, more positive values, of the abscissa should lie nearer to the right and of the ordinate nearer to the top.

4. For linear plots scales should be chosen such that the curve will, to the extent possible, have a geometrical slope in the neighborhood of unity. This allows both axis to be expanded to the largest extent possible as covered in step 3. For example the graph in Figure 1-7 approximates a slope of -1.

III. <u>Labeling the coordinate scales.</u> Main coordinate lines (or alternate ones) are labeled with the numerical values they represent. The name of the quantity represented is also given along each axis, together with the units in which it is measured. Each of the graphs contained herein illustrate this procedure.

IV. <u>Preparing a descriptive caption.</u> This should include a more or less complete description of what the graph is intended to show. The caption is usually included in an open region directly on the graph paper, or on the top of the graph paper. Both methods are illustrated through the graphs included in this unit.

V. <u>Plotting the data.</u> If the data plotted are subject to experimental or computational errors, each point should be surrounded by a suitable symbol, such as a circle. If at all practicable, it is customary to have the size of the symbol correspond approximately to the precision of the determination. See Figure 1-4 as an example of using circles to represent the uncertainty of a given value.

VI. <u>Fitting a curve to the plotted points.</u> In most cases in this course sufficient points will be available and the functional relation between the two variables will be well defined, so that a smooth curve may be drawn through the points. In general, inflections or discontinuities as seen in Figure 1-3 will be absent; if such irregularities are within experimental error, however, one must not ignore them
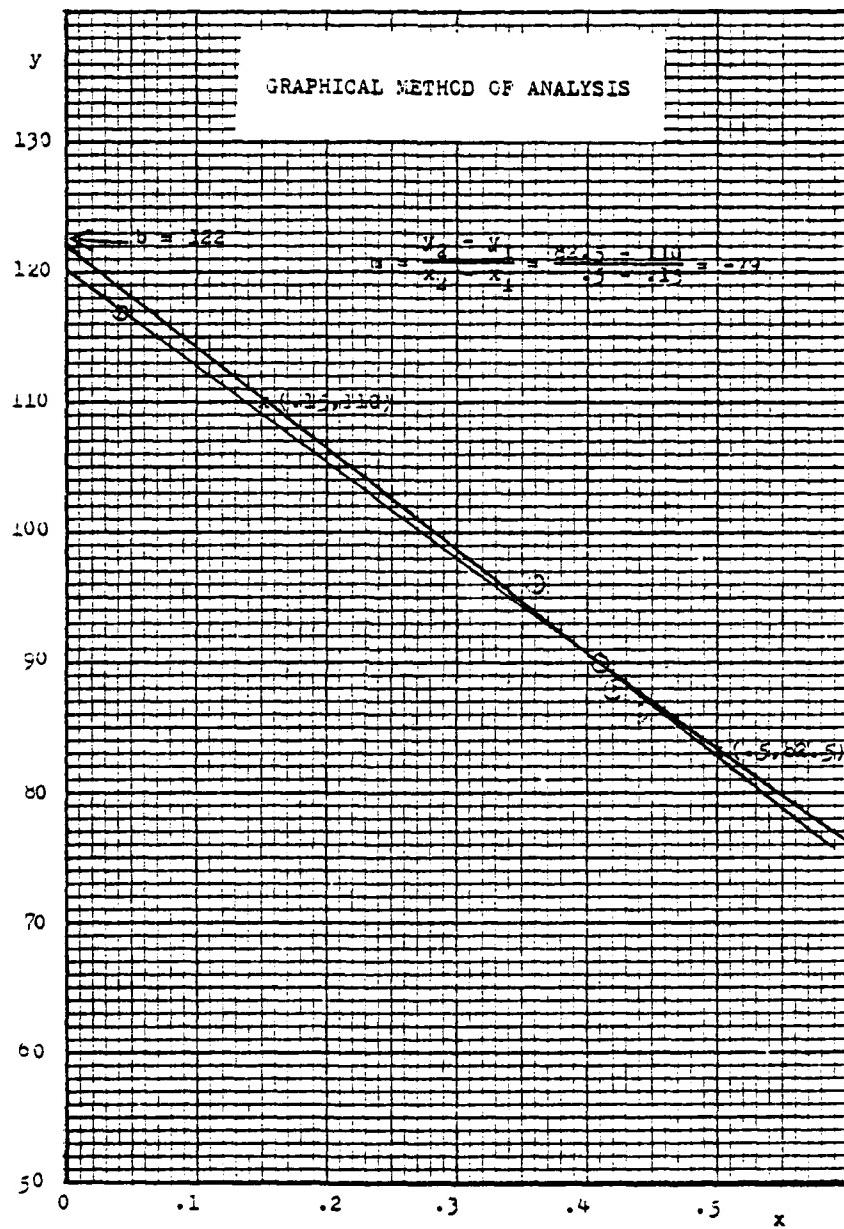
FIGURE 1-7. Calculation of slope and intercept from a graph.

by straining the curve, e.g., an inflection in a cooling curve (Freezing Point Diagram, Two-Component Alloy: Experiment 18, Crockford and Nowell 1956 p. 99.)

The curve should pass as close as reasonably possible to all the plotted points, though it need not pass through any single one. There is a natural tendency to over estimate the importance of the end points even though these <u>may</u> well be the least accurate points on the graph. This tendency should be avoided.

The remainder of the unit will discuss how to fit data and evaluate the resulting fit using (1) the graphical method, (2) the method of averages, and (3) the method of least squares. The method presented here will be dealing primarily with linear relationships, the types with which we will generally deal with in this course.

B. GRAPHICAL METHOD OF ANALYSIS

This method consists of visually examining the plotted data and "eye balling" the best curve to fit the data. It is probably the most frequently used method and is useful in the determination of slope and intercept. Much of the experimental data that you will collect in physical chemistry can be expressed in terms of linear relationships. In addition, many nonlinear relationships can be changed to linear relationships by performing simple mathematical operations like taking the logarithm of one variable and plotting it against the other variable. Problems 1-8 and 1-9 will give you practice in learning these important techniques. This method is exemplified in Figure 1-7.

EXAMPLE 1-14: One common example is the first order rate expression; $-dc/dt = kc$. If we integrate, we get the equation of a straight line;
$\ln c = -kt + \text{constant}$ which is equivalent to

$y = mx + b$, where $y = \ln c$, $m = -k$, $x = t$, and $b = \text{constant}$. A plotted set of data pairs for $\ln c$ versus t should give a straight line. By picking two representative points on this line we can calculate the slope, m, where:

$$m = \frac{\ln c_2 - \ln c_1}{t_2 - t_1}.$$

The constant, b, is equal to the intercept on the y-axis at the point where $t = 0$. In some cases it may be more convenient to calculate the intercept from the slope and the coordinates of a point on the line which for our example, $b = \ln c_1 - mt_1$. As an example see graph in Figure 1-4.

C. METHOD OF AVERAGES

Using paired values of x and y we can obtain simultaneous equations which can be used to solve for the slope and intercept. First the data is divided into two groups in such a way so as to reduce the data pairs to two points as far away from one another as possible. The greater the separation of the two points, the greater the precision of the straight line.

EXAMPLE 1-15:

Set 1			Set 2	
x	y		x	y
.04	117.0		.42	88.0
.36	96.0		.44	86.0
.41	90.0			

Using the above values of x and y we can write an equation for each set.

$$117 = .04m + b \qquad 88 = .42m + b$$
$$96 = .36m + b \qquad 86 = .44m + b$$
$$90 = .41m + b$$

Adding each set of points we have

$$303 = .81m + 3b \qquad 174 = .86m + 2b$$

Solving these last two equations simultaneously for m and b, we obtain m = -88 and b = 125. Using these values gives the equation y = -88x + 125. These calculations are based on the assumption that the deviation between the experimental value of y and the value calculated from the expression mx + b is zero.

D. METHOD OF LEAST SQUARES

We can perform a more rigorous treatment known as the method of least squares. However, two additional assumptions must be made. (1) "The fixed values of the independent variable are correct, and hence only the dependent variable is subject to errors of measurement; (2) The curve of best fit is the one which makes the sum of the squares of the deviations from the curve a minimum" (Crockford and Nowell 1975 p. 32). From the mathematical treatment of this method it is found that the best straight line is the one for which the slope, m, and intercept, b, are given by:

$$m = \frac{\Sigma x \cdot \Sigma y - n\Sigma xy}{(\Sigma x)^2 - n\Sigma x^2} \qquad \text{and} \qquad b = \frac{\Sigma xy \cdot \Sigma x - \Sigma y \cdot \Sigma x^2}{(\Sigma x)^2 - n\Sigma x^2}$$

Tables may be set up and calculation done by longhand or values for x and y may be entered into a preprogrammed calculator or computer.

When the three methods discussed above are compared using the data in Example 1-15, the results compare as follows:

	m	b
Graphical method	-79	122
Method of averages	-88	125
Method of least squares	-75.2	120.5

It should be noted that for the graphical method the values of m and b are the least certain since they are dependent on the "eye-balled" curve. This can be seen by looking at the graph in Figure 1-7. In this case both the slope and intercept are biased according to how the student draws the best line. It should also be noted that the method of least squares if not the best method is the method used the most often.

PRCBLEM 1-9: This problem illustrates how data can be represented. It involves the determination of the vapor pressure, P, of an organic liquid and the application of the Clausius-Clapeyron equation,

$$\frac{d \ln P}{dT} = \frac{\Delta H_v}{RT^2}, \quad \text{or} \quad \ln P = -\frac{\Delta H_v}{RT} + \text{Constant,} \quad \text{where}$$

ΔH_v is the amount of heat energy needed to vaporize a liquid.

For the data given below: 1. Plot P versus t^oC on rectangular coordinate graph paper. 2. Plot the logarithm of P versus 1/T K on rectangular coordinate paper or P versus 1/T K on semilogarithmic paper. 3. For number 2 calculate the slope, m, and the intercept, b, using the graphical method. 4. Make the same calculation using the method of averages. 5. Make the same calculation using the method of least squares. 6. Compare the three methods.

t^oC	$P_{mm}Hg$
15.0	59.0
20.5	77.4
25.8	98.4
29.1	114.4
33.0	135.4
36.4	156.4
39.1	176.4
41.9	197.4
44.1	214.4
46.7	236.9
48.5	253.9

PROBLEM 1-10: In order to use any of the three methods of graphical analysis, the variables being plotted must have a linear relationship. One of the "tricks," then, is to reformulate equations into a linear form as was done in Example 1-14. The following equations do not have a linear relationship between measured variables. Indicate how you would transform them and what you would plot to give a linear relationship so that the desired quantities could be found.

A. $\exp(\frac{A + BT}{T}) = P$

Measured variables are pressure, P, as a function of temperature, T. Solve for A and B. Which is the dependent variable and why?

IV. PROBLEMS SECTION

1. (Section III-B) Indicate how you would transform the following equation to a linear form and what you would plot to give a linear relationship so that the desired quantities can be found.

$$H = \frac{AP}{1 + TP}$$

H = is a measured variable
A = is a constant
P = is a measured variable
T = is the variable to be found

2. (Section I and II) Define the following terms:

a. Determinate error

b. Precision

c. Accuracy

d. Significant figure(s)

e. Average error

f. Standard deviation

g. Probable error

3.   (Section II-E)

The current is determined in a circuit by measuring the voltage drop across two resistors in series.
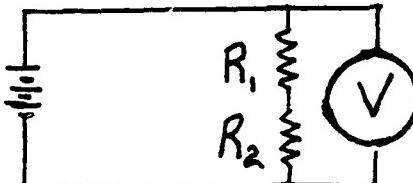
a.   If R_1 is a 300 ohm ($\pm$ 5%) resistor and R_2 is a 100 ohm ($\pm$ 1%) resistor and the voltmeter reads 2.5 volts and is accurate to $\pm$ .01 volts, what is the value of the current, I, and what is the maximum uncertainty (error) in I?   (For resistors in series the total resistance is the sum of the individual resistances.)   Use Ohm's law, E = IR, where E is the voltage, I is the current, and R is the resistance.

b.   What contributes most to the maximum uncertainty, the uncertainty in R_1, the uncertainty in R_2, or the uncertainty in E?   Show how you arrived at that conclusion.

4.   (Significant Figures, SF, - Section I-C)   A sample of gas weighing 1.602 g occupies 224 mL at a pressure of 749 mm Hg and a temperature of 100.0°C.   Calculate the molecular weight (M) of the gas, using the equation:

$$M = \frac{gRT}{PV}.$$ (NEGLECT ERROR CALCULATION UNTIL #5)

where   g = mass in grams
         T = temperature in K
         P = pressure in atm.
         V = volume in mL
         R = gas constant = 82.06 mL-atm/mole-K
                            ANS: 222 g/mole - 3SF

5. (Section II-E) <u>Estimate</u> the error in each of the variables and calculate the total error for Problem #4.

6. (Statistical Methods - Section II) A student on analyzing a sample compound for the percentage of bromine makes four trials with the following results:

$$36.0, \quad 36.3, \quad 35.8, \quad \text{and} \quad 36.3 \ \%.$$

Calculate:
   a. The arithmetic mean
   b. The average error
   c. The standard deviation
   d. The probable error

7. Using the ideal gas law equation, $n = PV/RT$, where $P = 460 \pm 1$ torr, $V = 147 \pm 1$ mL, $T = 29.0 \pm 0.5^{\circ}C$, find the value of n, the number of moles, and the associated error.

ANS: $n = 3.59 \pm 0.04$ moles

8. Find the error in <u>k</u> given by the equation $k = Ae^{-E/RT}$ where

$A = 4.5 \times 10^{11} \pm 0.1 \times 10^{11}$, $E = 3.56 \pm 0.05$ kcal/mole, and $T = 27.0 \pm 0.5^{\circ}C$.

ANS: $K = 1.15 \times 10^{9} \pm 0.04 \times 10^{9}$

9. For each of the following write a linear form and indicate how the constants can be evaluated from a graph:

a. $y = ae^{bx}$

b. $a/x + b = y$

c. $1/y = bx^{2}$

d. $y = ab^{x}$

APPENDIX B

DETERMINATION OF THE MOLECULAR WEIGHT OF A
VOLATILE SUBSTANCE: THE VICTOR
MEYER METHOD

APPENDIX B

DETERMINATICN CF THE MCLECULAR WEIGHT CF A VCLATILE
SUBSTANCE: THE VICTCR MEYER METHCD

I. THEORY

The ideal gas law can be rearranged into the form
$M = wRT_2/P_2V_2$, where M is the molecular weight of the gas.
We can obtain a value for M if we can weigh the amount of
gas w which is required to fill the volume V_2 at a
temperature T_2 to a pressure P_2; if other gases or vapors
are present, P_2 represents the partial pressure of the gas
whose M is being determined.

In this experiment the molecular weight of a volatile
substance is determined approximately by considering the
vapor to be a perfect gas and measuring the volume of air
displaced by a known weight of the vapor. The "air"
displaced is measured over water so a correction must be
applied to the total pressure of the confined gases in order
to determine pressure exerted by the "air" alone. The term
"air" includes some water vapor as determined by measuring
the relative humidity.

II. PRCCEDURE

The apparatus is shown in the diagram on the next page; the
various parts will be referred to by the letters on the
diagram.

a. Fill the bottom bulb of B with water and start to heat
with a bunsen burner. Place a thermometer near the
measuring buret E.

b. Remove glass rod C and tube D from the volatilization
chamber A and flush A with air by pulling the air out of A
with a glass tube connected to an aspirator.

c. Add tap water to measuring buret E and level bulb F
until the bulb is approximately half full when level is at
zero on measuring buret.

d. Make certain stopcock G is well greased.

e. Form bulblet H by sealing one end of a 5 mm soft glass
tube and pulling a capillary on the other end. The bulblet
should be about 1 inch long and the capillary should be
small enough to pass through the hole I in tube D. Bend the
capillary at right angles.

f. Weigh the bulblet (w_1) to the nearest 0.1 mg.

FIGURE 6-1
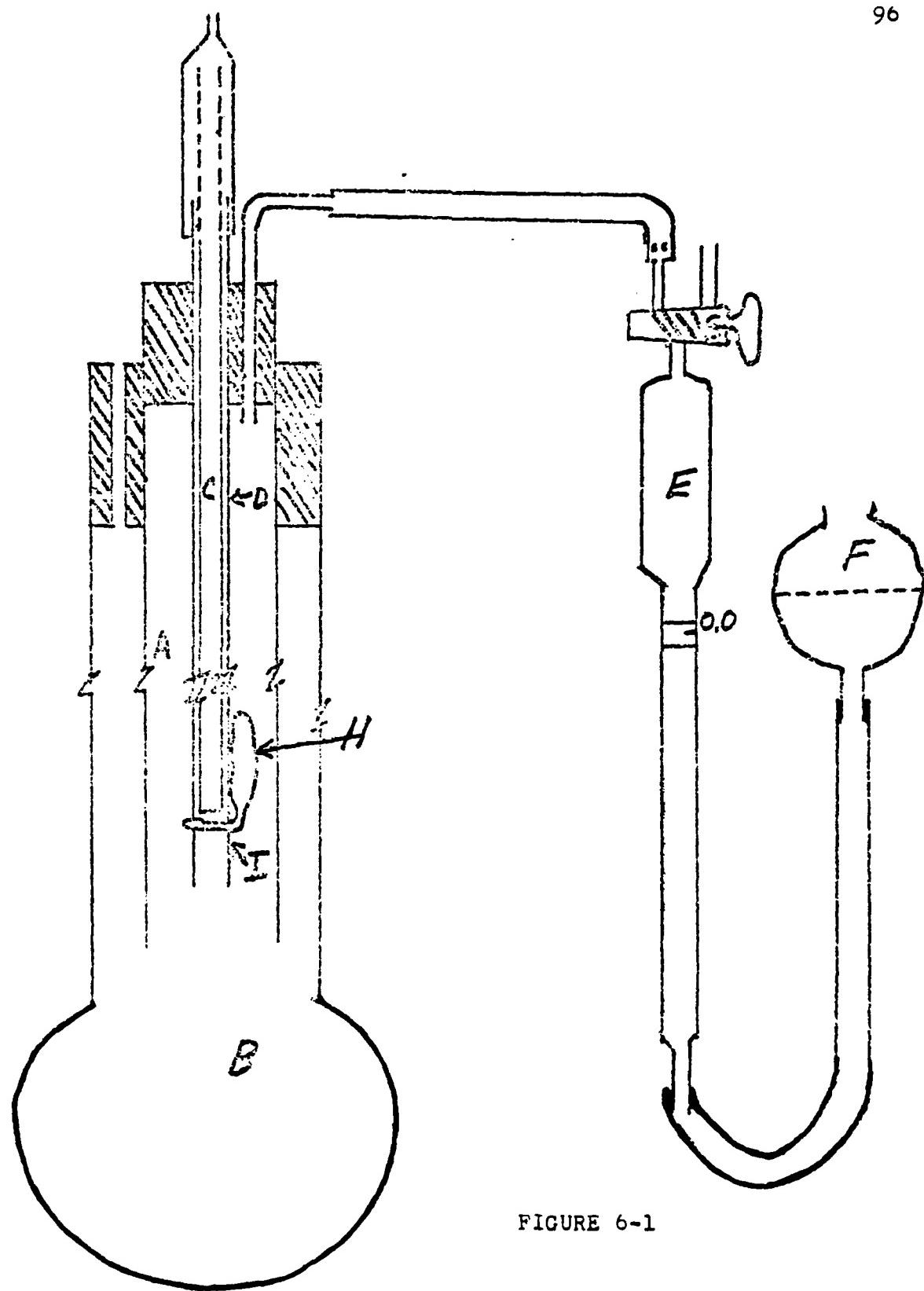
g. Fill the bulblet with the liquid whose molecular weight is to be determined (if the molecular weight is known, the approximate amount of liquid needed may be calculated to give a volume near the capacity of the buret). Heat the bulblet gently in a flame and dip the capillary into the beaker of liquid while the bulblet cools. Some liquid will be drawn in, which will vaporize and drive the air out if the bulb is again heated. After this second heating, dip the capillary into the liquid while the bulb cools.

h. Seal the capillary by heating and pulling off the tip. Weigh the filled bulblet and tip to the nearest 0.1 mg. (w_2)

i. Place the bulblet in tube D at I and place C and D into chamber A. The bulblet may be held in a vertical position with a rubber band.

j. Open G to A and with water in B boiling at a constant rate, equilibrate the water levels in F and E. After equilibrium has been established, read the measuring buret E (V_1). This reading should be close to zero. The reading may be adjusted by drawing in or pushing out air through G.

k. Break the bulblet by pushing the glass rod C down upon the capillary. The liquid will vaporize and force air out of chamber A. As the water level falls in E, lower F to keep the water levels equal. This prohibits the pressure from increasing which may cause joints to leak.

l. When a maximum volume is reached with water levels in E and F equal, shut off G. If G is left open too long some vapor will enter the cooler parts of the apparatus and condense.

m. Allow the gas in E to come to room temperature and to become saturated with water vapor. This state is attained when the reading on the buret remains constant. Read the buret when the water levels are equal (V_2).

n. Record the temperature (T_1) outside the buret, the barometric pressure (P_b), and the temperature of the barometer each time a sample is run. Record the relative humidity of the atmosphere.

o. Clean apparatus and return to storeroom.

III. CALCULATIONS

Calculate the approximate molecular weight (M_1) of the unknown using the perfect gas equation. A good approximation for the pressure of the air forced from the volatilizing chamber is:

$$P_a = P_b - P_{H_2O} \, (1-r.h./100)$$

where P_b equals the barometric pressure, P_{H_2O} equals the vapor pressure of water at T_1 , and r.h. is the relative humity.

IV. TREATMENT OF ERRORS

Estimate the errors in the laboratory observation and calculate the absolute error in M_2.

Name:_____ Date:_____

V.	DATA and RESULTS	Run 1	Run 2
1.	Weight of bulblet	g	g
2.	Height of bulblet and liquid	g	g
3.	Cbserved barometric pressure at start	mm Hg	mmHg
4.	Reading of barometer thermometer	$^{\circ}$C	$^{\circ}$C
5.	Corrected pressure at start (P_s)	mm Hg	mmHg
6.	Apparent temperature of gases	$^{\circ}$C	$^{\circ}$C
7.	Constant correction No._____	$^{\circ}$C	$^{\circ}$C
8.	Corrected temperature of gases (T_1)	$^{\circ}$C	$^{\circ}$C
9.	Buret reading at start (V_1)	mL	mL
10.	Buret reading at finish (V_2)	mL	mL
11.	Cbserved barometric pressure at finish	mm Hg	mmHg
12.	Reading of barometer thermometer	$^{\circ}$C	$^{\circ}$C
13.	Corrected pressure at finish (P_f)	mm Hg	mmHg
14.	Temperature of wet bulb	$^{\circ}$F	$^{\circ}$F
15.	Temperature of dry bulb	$^{\circ}$F	$^{\circ}$F
16.	Relative humidity	%	%

. . . .

17.	Weight of liquid	g	g
18.	Volume of air displaced	mL	mL
19.	Average pressure ($P_s + P_f/2$) = P_b	mm Hg	mmHg
20.	Vapor pressure of water at T_1	mm Hg	mmHg
21.	Pressure of air displaced	mm Hg	mmHg
22.	Molecular weight of unknown		
23.	Absolute error in molecular weight		

APPENDIX C

ADIABATIC CALORIMETRY

GUIDELINES FOR THE PREPARATION OF LABORATORY REPORTS

The following is an outline of what you should include in your laboratory reports. The material should be presented in the order listed, and your reports should be typewritten or neatly hand-written. Failure to follow these guidelines or turn the report in at the specified time will result in the student receiving less than full credit for the report.

1. TITLE PAGE (See sample on next page)

2. OBJECTIVE - A concise statement of the purpose of the experiment.

3. DRAWING - A diagram or schematic of any unusual equipment with the purpose of showing how it works and its construction.

4. DISCUSSION OR THEORY - A concise review of the theory.

5. PROCEDURE - Simplified description of the procedure used.

6. BIBLIOGRAPHY - Citation of references following ACS guidelines.

7. DATA - The data sheet provided with a given experiment should be turned in with your report.

8. CALCULATIONS - A sample calculation of each type of calculation should be given in the order requested in the report. The instructor may request you to include maximum error calculations for many of the experiments.

9. RESULTS - The results should include the concise reporting of your results together with their expected uncertainties, units, and a comparison with literature values.

10. CONCLUSIONS - A short discussion of your results, i.e., why they did not agree with the literature values, and overall conclusions.

11. GRAPHS AND COMPUTER PRINTOUTS - These should be included whenever applicable at the end of the report. They should be completely labeled and separately identified for easy reference.

12. PROBLEMS - Assigned problems should be completed and placed at the end of the report.

(TITLE PAGE)

COURSE_____INSTRUCTOR_____

EXPERIMENT TITLE_____

EXPERIMENT NUMBER_____

DATE PERFORMED_____

DATE SUBMITTED_____

DATE DUE_____

GRADE_____

NAME_____

PARTNER'S NAME_____

APPENDIX C

EXPERIMENT 2 - ADIABATIC CALORIMETRY

A. STUDY GUIDE AND REVIEW ASSIGNMENT

1. Read section(s) on calorimetric measurements in your
lecture textbook prior to lab. This should give you a short
overview of thermochemistry and calorimetry.

2. Work the following problems which were taken from
Daniels and Alberty (1975, p. 36 and p. 38):

a. In an adiabatic calorimeter, oxidation of 0.4362
gram of naphthalene caused a temperature rise of 1.707°C.
The heat capacity of the calorimeter and water was
2460 cal/K. If corrections for oxidation of the wire and
residual nitrogen are neglected, what is the enthalpy of
combustion of naphthalene per mole?   Ans.   -1234 kcal/mol

b. The combustion of oxalic acid in a bomb calorimeter
yields 673 cal/g at 25°. Calculate ΔU° and ΔH° for the
combustion of 1 mole of oxalic acid (M = 90.0).
      Ans. ΔU° = -60.57 kcal/mol, and ΔH° = -59.68 kcal/mol

If necessary see your instructor for help with these problems.

3. Read the THEORY section and PROCEDURE section of this
experiment and complete this part of your report prior to
coming to class.

4. Supply definitions for the KEY WORDS in your report.
The majority of these terms are discussed in the THEORY
section and in your lecture textbook.

5. Complete the PRELIMINARY REPORT on the next page prior
to class.

6. Read the section in the Parr Adiabatic Calorimeter
manual pertaining to loading the bomb. Check with your
laboratory instructor concerning the location of the manual.

B.   OBJECTIVES - You shall be able to:

1.   Define and/or briefly discuss the KEY WORDS including appropriate equations.

2.   Summarize in writing how one determines heats of combustion.

3.   List the corrections to be made in making the calculations in order to obtain the most accurate value.

4.   Calculate the thermodynamic values for ΔH and ΔU as shown in the EXAMPLE section.

5.   Derive Equation 2-7 and explain its significance.

C.   KEY WORDS: (Supply equations where possible.)

Adiabatic

Calorimetry

Enthalpy, ΔH

First law of thermodynamics

Heat Capacity at constant volume, C_v

Heat Capacity at constant pressure, C_p

Heat, Q

Heat of Combustion

Internal Energy, ΔU

Units of energy and their conversions, e.g., 1 calorie = 4.184 joules

Work, W

D.   PRELIMINARY REPORT - Answer the following questions
prior to coming to the laboratory. You may be required to
turn this sheet in for grading or you may have a quiz prior
to performing the experiment.

1.   Why is 1 mL. of water added to the bomb?

2.   How tightly should the bomb head be turned when replaced
on the bomb?

3.   What is the maximum weight of the benzoic acid sample?
Why?

4.   What is the maximum time that the ignition button can
be depressed?   Why?

5.   Why is the temperature of the water jacket kept as
close as possible to the temperature of the water in the
bucket during an actual run?

6.   What is a fuse wire correction?

7.   What compound will be used as a standard for calorimeter
calibration?

8.   Name one use of the thermodynamic results one obtains
from an experiment of this type.

E. REFERENCES

1. Daniels, F., R. A. Alberty, "Physical Chemistry," John
Wiley & Sons, Inc., 1975, pp. 22-23.

2. Daniels, et al., "Experimental Physical Chemistry,"
McGraw-Hill, New York, p. 18, 1970.

3. Metz, Clyde R., "Theory and Problems of Physical
Chemistry," McGraw-Hill, New York, p. 38, 1976.

4. Parr Adiabatic Calorimeter Manual, Parr Co., Moline Ill.

F. APPARATUS AND CHEMICALS

Your instructor should have the following equipment located
in one area: The Parr Adiabatic Calorimeter with assoc-
iated parts and instruction booklet; pellet press; two
special thermometers calibrated in 0.01° intervals; fuse wire;
burette, beakers, stand, and clamp; cylinder of oxygen;
benzoic acid of high purity, naphthalene, and/or other
samples; 0.0725 N sodium hydroxide, or other standard base;
and phenolphthalein or some other appropriate indicator.

G. PURPOSE

This experiment is to determine (1) the heat capacity of
your calorimeter, and (2) the heat of combustion of some
materials using a Series 1200 Parr Adiabatic Calorimeter,
the cross section of which is shown in Figure 2-1.

H. THEORY

Calorimetry is the measurement of the quantity of
heat evolved or absorbed during a process. Under the newly
adopted system of units (SI) the unit of energy is the joule,
J, where one calorie, (the old unit in the metric system)
equals 4.184 joules. However, the calorie is still in
common usage.

This discussion will be limited to a brief descrip-
tion of the operation of a calorimeter. All commercial
instruments, including calorimeters, are accompanied by
detailed instructions, and it is necessary that the student
consult these before using the instrument. Figure 2-1, in
this section, gives a cross sectional view of an adiabatic
calorimeter.

A typical calorimeter consists of a reaction chamber
surrounded by a jacket. For combustion reactions the
chamber is usually a rigid walled container called a bomb.
The bomb is submerged in a known amount of water. The
water is contained in apparatus equipped with a thermometer
and stirrer. For this experiment the reaction takes place
at constant volume, isochoric conditions, in a stainless

steel bomb (Figure 2-1). The sample is ignited in an oxygen atmosphere by contact with a hot wire. The heat generated by combustion raises the temperature of the bomb, its contents, and the water in the bucket. The bucket, bomb, and its contents constitute the reaction chamber, i.e., the calorimeter system. The measurement may be either adiabatic or nonadiabatic. You will perform the adiabatic reaction.

The adiabatic procedure consists of maintaining the same temperature in the water jacket as in the bucket so that there is no heat transfer, and all the heat of reaction goes into changing the temperature of the reaction chamber. As the temperature of the reaction chamber changes, the temperature of the jacket is changed so that it parallels that of the reaction chamber. This is accomplished by carefully adding small amounts of hot or cold water slowly into the jacket.

In using any calorimeter, it is necessary to obtain the heat capacity of the calorimeter system. The heat capacity is the number of calories necessary to raise the temperature of the entire calorimeter system by $1^\circ C$. This is found by burning a known amount of a substance having a known heat of combustion. Benzoic acid of high purity is usually employed. The temperature rise due to the sample is accurately determined, and the number of joules of heat released in the combustion is calculated. These two values enable one to calculate the heat capacity of the calorimeter system. This is then used in determining the heat of combustion of any other substance.

In the determination of the heat of combustion with a bomb calorimeter, it must be remembered that the measurement is made at constant volume, not at constant pressure. Therefore, the heat of combustion determined is ΔU rather than ΔH.

Since the primary purpose of these experiments is to teach physical chemistry concepts, students should understand what is meant by ΔU. We know that a given amount of substance possesses energy. This is associated with translational, vibrational, rotational, nuclear, and electronic energies of molecules. With the exception of translational energy, these forms of energies are concerned with internal processes, and they are collectively called internal energy, U. However, it is impossible to measure the total energies, and we cannot say that a particular substance has an internal energy of so many joules. Fortunately, we are not interested in the absolute internal energy, but rather in changes in it when a process occurs. We refer to such a change as internal energy, ΔU.

This brings us to the first law of thermodynamics which is in reality the law of conservation of energy. It can be stated in many ways, but the most common way is: ENERGY CANNOT BE CREATED OR DESTROYED. In most of the cases of interest to the chemist, as in this experiment, only heat, work, and internal energy are involved. By the convention

used throughout this study, we say that when heat is absorbed by the system, it is positive and when work is done by the system, it is positive. If Q joules of heat are supplied to a gaseous system in equilibrium, which is not restricted to a constant volume, the gas will expand and do W joules of work. If all the heat is not converted to work, the system takes up the heat internally by increasing the movement of its molecules and other internal energies, i.e., there is an increase in internal energy, ΔU. Since by the first law energy cannot be lost, the internal energy must be due to the heat supplied and the work done. This gives us the first law equation which may be applied to the calorimetric process,

$$\Delta U = Q - W \qquad (2-1)$$

Since the experiment is carried out under adiabatic conditions, Q = 0 for the calorimeter and its contents. Since the volume is constant, and no non-mechanical work is done, W is also zero. Therefore, ΔU = 0.

In general we can calculate ΔU in two ways. The more direct way is to measure the amount of electrical work required to produce a temperature change, ΔT, in the calorimeter plus products. Since Q = 0, W (electrical) = ΔU. Alternatively, since

$$\Delta U = -C_v \Delta T \qquad (2-2)$$

over a small temperature range in which C_v is constant, a reaction of known ΔU can be carried out and C_v calculated and then used to calculate ΔU for some other system. This is exactly what is done in this experiment. (See Problem 2-8)

There are, however, other contributions to ΔU besides the heat of combustion of the sample. These are due to the burning of the fuse wire and the formation of nitric acid from the nitrogen of the air trapped inside the bomb. In the experiment water is added to the bomb to absorb the HNO_3 produced. Therefore,

$$N_2 + 5/2\ O_2 + H_2O \longrightarrow 2HNO_3. \qquad (2-3)$$
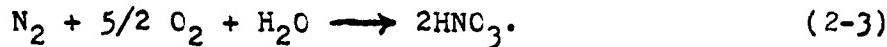
The total contributions give (See EXAMPLE 2-3)

$$C_v \Delta T = -\Delta U_{sample} - \Delta U_{wire} - \Delta U_{HNO_3} \qquad (2-4)$$

Frequently, you are asked to calculate the enthalpy, ΔH, from experimental values of ΔU, as in this experiment. For a constant pressure process in which the only work is against the pressure of the surroundings

$$W = -P\Delta V.$$

Substituting this equation in Equation 2-1 and rearranging gives

$$Q_p = \Delta U + P\Delta V.$$

But since the pressure is constant, we can add $V\Delta P$ to the right side without effecting the equality and obtain:

$$Q_p = \Delta U + P\Delta V + V\Delta P$$

$$= \Delta U + \Delta(PV)$$

$$= \Delta(U + PV).$$

But since U, P, and V are state functions, U + PV must be a state function. We call this sum the enthalpy, and represent it by the symbol H. The equation can be written as

$$\Delta H = \Delta U + \Delta(PV), \qquad (2-5)$$

and we see that $Q_p = \Delta H.$

The quantity $\Delta(PV)$ is sufficiently small for reactions involving solids and liquids that changes in $\Delta(PV)$ can be neglected and $\Delta(PV)$ values for gaseous reactants and products need be considered. (See EXAMPLE 2-1) If the gases can be approximated as ideal, then assuming constant temperature

$$\Delta(PV) = \Delta(nRT) = \Delta n(RT) \qquad (2-6)$$
and
$$\Delta H = \Delta U + \Delta n(RT) \qquad \text{(See PROBLEM 2-9)} \qquad (2-7)$$

where Δn is the change in the number of moles of gas in a reaction. For

$$C_6H_5COOH_{(s)} + 15/2\ O_{2(g)} \longrightarrow 7\ CO_{2(g)} + 3\ H_2O_{(1)} \qquad (2-8)$$
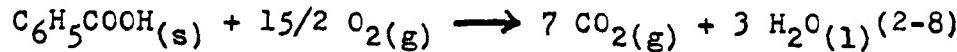
$$\Delta n = 7-7\tfrac{1}{2} = -\tfrac{1}{2}.$$

I. EXPERIMENTAL PROCEDURE - The instructor should demonstrate the procedure. The student should be sure to read the SAFETY PRECAUTIONS in section J before proceeding.

1. Weigh out approximately 1 gram of benzoic acid, but no more than 1.1 grams.

2. Weigh a metal combustion capsule to the nearest 0.1 mg. Be sure to handle with forceps. Using a pellet press prepare a pellet of benzoic acid. Have the instructor demonstrate the procedure for preparing a pellet. Place the pellet in the capsule and reweigh. Be sure the pellet weighs no more than 1.1 g.

3. Fill a 2000 mL volumetric flask to the 2000 gram mark and cool the flask to 20°C. For greater accuracy the student can weigh out the water.

4. Remove the head from the bomb. Never place the head of the bomb anywhere except on the support stand provided (See manual) or in the bomb itself.

5. Accurately measure 10.0 cm of fuse wire. Following the diagram in Figure 2-2 (See page 28 of manual) carefully attach the fuse wire in the bomb head. Place the pellet and pellet capsule in holder. Insure the fuse wire rests on the sample holding it against the capsule. Tip the capsule slightly.

(Both FIGURES are taken from; Crockford et al., "Laboratory Manual of Physical Chemistry," John Wiley, New York, 1975, pp. 110 and 111.)
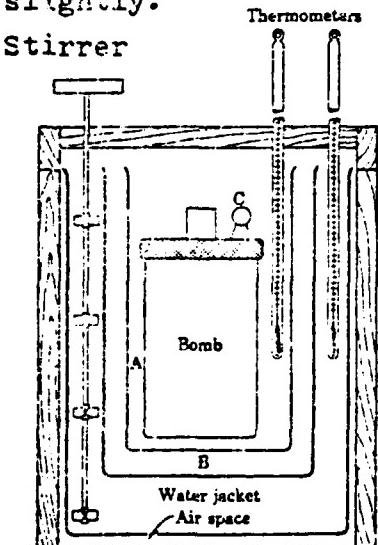
A - Water jacket
B - Air jacket
C - Electrical connection
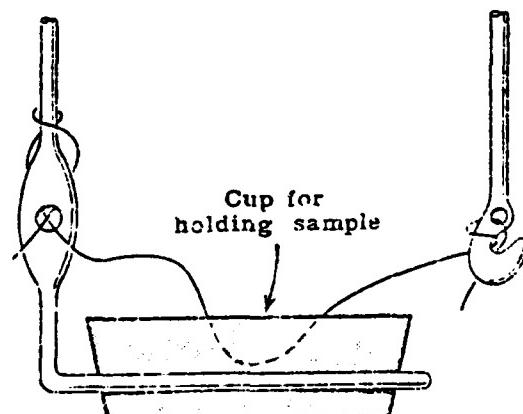
Figure 2-1. Cross section--adiabatic calorimeter. (Courtesy of Parr Instrument Company, Moline, Ill.)

Figure 2-2. Method of binding fuse wire. (Courtesy of Parr Instrument Company, Moline, Ill.)

6. Pipette 1.0 mL of distilled water into the bomb.

7. Carefully replace the bomb head, firmly tighten the screw cap. Be certain not to jar or tip the bomb in any way so as to disturb the sample. Close the needle valve firmly and slowly fill with 30 atmospheres of oxygen. DO NOT OVERFILL. Check for leaks by applying a soap solution to possible leak positions.

8. Add the 2000 g of distilled water to the bucket. Allow 1 minute draining time. Place bucket in the Parr calorimeter, stirrer to the rear. Carefully place the bomb in the bucket, over the raised portion of the base on the bottom of the bucket. Attach the terminal to the electrical post on the top of the bomb. Be sure to shake back any water adhering to your fingers.

9. Close the calorimeter, lower the thermometers and start the stirring motor.

10. Adjust the temperature in the jacket to or slightly lower than the calorimeter temperature. Allow 5 minutes for equilibrium. Thermometers should read to within 0.01°F. Record the temperature of both thermometers using the magnifying glasses provided.

11. Ignite the sample at a distance by depressing the button on top of the ignition box. Watch for the red light and release. Under no circumstances should the button be pressed for more than 5 seconds! The series resister will burn out and the ignition unit will no longer pass current.

12. In approximately 20 seconds the calorimeter temperature will begin rising. Hot water must be added to the jacket to keep pace with the calorimeter. Adjust the final temperature of the jacket to within 0.01° of that of the bucket. The maximum temperature of the bucket should remain constant for at least 3 minutes. Record the temperature.

13. Stop the stirring motor and wait 10 to 15 seconds before opening the lid. Be sure to raise the thermometers first. Open the lid and remove the bucket and bomb. Release the pressure slowly from the bomb.

14. Wash all interior surfaces of the bomb quantitatively with distilled water. Collect the washings in a beaker or flask. Titrate the dissolved HNO_3 with 0.0725 $\underline{N}$ base. Be sure to add an appropriate indicator.

15. Remove the unburned pieces of fuse wire, straighten and accurately measure them.

16. Dry the inside of the bomb and bucket thoroughly before proceeding.

17. Repeat the above process using a 0.6 to 0.75 g sample pellet of napthalene. The napthalene should be powdered with a mortar and pestle before the pellet is made. Use a new metal capsule (cup).

18. Leave the head of the bomb in the support stand and dry the bomb and bucket at the end of the experiment.

19. Fill in one copy of a data sheet to the dotted line and turn in to your instructor prior to leaving class. (This is at the discretion of the instructor.)

J. SAFETY PRECAUTICNS

1. Do not overload the bomb with oxygen.

2. Do not use a sample that is too large.

3. Stand back from the calorimeter when igniting the bomb.

4. Follow ignition procedures carefully.

5. Handle thermometers with great ease. Make certain that they are raised high enough to clear the body of the calorimeter when the cover is being opened or closed.

6. Do not turn off water supply to the heater before unplugging the heater.

7. Make certain the stirrer shafts mesh while the calorim- eter cover is being closed.

8. Do not use any wrenches on the bomb.

9. Do not fire the bomb if gas bubbles are leaking from it when it is submerged in water.

K. CALCULATICNS - See the EXAMPLES as an aid in making the calculations and in solving the problems.

In performing the calculations, it should be noted that the temperature rise is due to the combustion of the sample, the burning of the fuse wire, and the formation of the nitric acid. Thus in determining the heat capacity of the calorimeter add together the heat contributed by the burning wire, the formation of the nitric acid, and the combustion of the benzoic acid. Then divide this sum by the observed temperature rise in order to obtain the heat capacity of the calorimeter.

In the determination of the heat of combustion of the assigned sample, multiply the net temperature rise by the heat capacity of the calorimeter and then subtract the

effects due to the burning of the wire and the formation of
nitric acid. Divide the corrected total by the actual
weight of the sample to obtain the heat of combustion of a
one gram sample. Convert this to a value per mole. Finally,
you can calculate the heat of combustion at constant pressure
by use of Equations 2-7 and 2-8.

In your laboratory report show how the following
calculations are made. MAKE ALL YOUR CALCULATIONS IN TERMS
OF JOULES OR KILOJOULES. The calculations asked for can
not necessarily be done in the order given below.

1. The correction term due to the burning of the fuse wire
at -9.62 J/cm.

2. The correction term due to the formation of nitric acid
at -57,700 J/mole.

3. The term corresponding to the combustion of the sample.

4. Calculate the total heat capacity of the calorimeter
(bomb and contents, 2000 g of water, and container).

5. Calculate both ΔU and ΔH for the combustion of one mole
of naphthalene or other sample at the temperature range of
your reaction.

6. Perform a maximum error analysis treatment on ΔH of
your sample as outlined in UNIT I.

7. The problems at the end of the experiment should be
included at the end of the report.

L. EXAMPLES AND PROBLEMS

EXAMPLE 2-1: (Metz, 1976, p. 33) The heat of combustion of $H_{2(g)}$ to form $H_2O(l)$ under constant pressure conditions is -68.32 kcal/mole at 25°C. If the water is formed at 1 atm and has a density of 1.00×10^3 kg/m³, calculate ΔU for the reaction.

For the reaction

$$H_{2(g)} + \tfrac{1}{2}C_2 = H_2O_{(1)} \qquad \Delta H = -68.32 \text{ kcal}$$
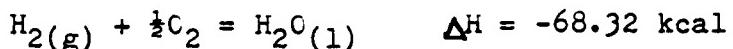
The term $\Delta(PV)$ in $\Delta H = \Delta U + \Delta(PV)$ is calculated as follows:

$$\Delta(PV) = \Sigma(PV)_{Products} - \Sigma(PV)_{Reactants}$$

$$\Sigma(PV)_{Products} =$$

$$(1 mole)(1 atm)(0.018 \text{ kg/mole})(1000 \text{ kg/m}^3)(101,325 \text{ J/(m}^3\text{atm}))$$

$$= \underline{1.82 \text{ J}} = \underline{1.82 \times 10^{-3} \text{ kJ}}$$

$$\Sigma(PV)_{Reactants} = nRT \text{ since they are gases}$$
$$= \tfrac{3}{2}RT$$
$$= \tfrac{3}{2}(8.314 \times 10^{-3} \text{ kJ/(mole-K)})(298 \text{ K}) = \underline{3.72 \text{ kJ}}$$

As seen above the $\Delta(PV)$ term for the liquid phase can be neglected while the $\Delta(PV)$ term for gases can be replaced by $\Delta n(RT)$ giving $\Delta H = \Delta U + \Delta n(RT)$ where Δn is determined using the coefficients of the gaseous substances only.

$$\Delta U = \Delta H - \Delta(PV)$$
$$= (-68.32 \text{ kcal})(4.184 \text{ kJ/kcal}) - (1.82 \times 10^{-3} - 3.72)\text{kJ}$$
$$= -285.85 - (-3.72)$$
$$= \underline{-282.13 \text{ kJ}}.$$

EXAMPLE 2-2: (Metz, 1976, p. 40) What would be ΔH for the combustion of benzoic acid at 25°C if $Q = -6316$ cal/g under isochoric conditions?

The value of Q under isochoric conditions is equal to ΔU, so for 1 mole of benzoic acid

$$\Delta U = (-6316 \text{ cal/g})(122.13 \text{ g/mole})(4.184 \text{ J/cal}) = -3227 \text{ kJ/mole}$$

For the reaction

$$C_6H_5COOH_{(s)} + 15/2 \; C_2 = 7CO_{2(g)} + 3H_2O_{(1)}$$
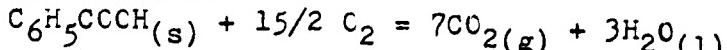
$$\Delta U = -3227 \times 10^3 \text{ kJ/mole}$$

$\Delta n = -\tfrac{1}{2}$, therefore, $\Delta H = -3227 \text{ kJ} + (-1 \text{ kJ}) = -3228 \text{ kJ/mole}$.

EXAMPLE 2-3: To calibrate a calorimeter 1.0039 grams of benzoic acid were oxidized producing a temperature change of $4.695^\circ F$. The nitric acid produced was titrated with 10.8 mL of 0.0725 molar NaOH. A total of 8.0 cm of fuse wire was consumed at the rate of 2.3 cal/cm. If ΔU°_{298} for the oxidation of benzoic acid is -6318 cal/g, calculate the heat capacity of the calorimeter, C_v.

For the combustion reaction, assume the calorimeter constant is temperature independent and consists of terms contributed by the heat of combustion of benzoic acid, the burning of the fuse wire, and the contribution from formation of nitric acid. Since for this process $\Delta U_{Total}=$ $0 = \Delta U_{Constant\ T} + \int C_v dT$ (See Theory Section page 6)

Then $\Delta U_T = -\int C_v dT = -C_v \Delta T$

$$C_v = \frac{-\Delta U_{sample}}{\Delta T} - \frac{\Delta U_{wire}}{\Delta T} - \frac{\Delta U_{HNO_3}}{\Delta T}$$

$\Delta U_{Sample} = (1.0039g)(-6318 cal/g)(4.184 J/cal) = -26.54\ kJ$

$\Delta U_{Wire} = (8.0\ cm)(-2.3\ cal/cm)(4.184 J/cal) = -0.077\ kJ$

For a neutralization reaction as between HNO_3 and NaOH, -13,800 cal/mole are liberated. Therefore,

(0.0725 moles/liter)(1 liter/1000 ml)(-13800 cal/mole) =

-1.00 cal/mL

and $\Delta U_{HNO_3} = (10.8\ ml)(-1.0\ cal/mL)(4.184\ J/cal) = -0.045\ kJ$

$$C_v = \frac{26.54 + 0.077 + 0.045}{4.695} = \underline{5.68\ kJ/^\circ F}.$$

EXAMPLE 2-4: (Metz, 1976, p. 51) One of the uses for heats of combustion is calculating heats of reaction for use in Hess's Law,

$$\Delta H_R = \Delta H_{Products} - \Delta H_{Reactants}.$$

For the following at $25^\circ C$,

$Fe_{(s)} + \frac{1}{2}O_{2(g)} = FeO_{(s)}$ $\Delta H = -65.0\ kcal$

$2Fe_{(s)} + \frac{3}{2}O_{2(g)} = Fe_2O_{3(s)}$ $\Delta H = -197.0\ kcal$

predict ΔH_R for

$2FeO_{(s)} + \frac{1}{2}O_{2(g)} = Fe_2O_{3(s)}.$
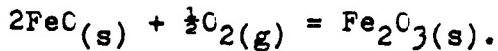
$\Delta H_R = -197.0 - (2(-65.0) + 0) = \underline{-67.0\ kcal}$

PROBLEM 2-1: (Labowitz & Arents, 1969, p. 30) A student made the following erroneous statement in a laboratory on bomb calorimetry: "$\Delta H = \Delta U + P\Delta V$. Since the bomb calorimetry process is a constant volume one, $\Delta V = 0$, and $\Delta U = \Delta H$." Explain why this argument is incorrect.[1]

PROBLEM 2-2: What would be the effect on your calculation of heat capacity of the calorimeter if you ignored the contribution due to the fuse wire and the formation of HNC_3?

PROBLEM 2-3: Which measurement in this experiment introduces the largest error? (HINT: Use maximum error calculations introduced in UNIT on treatment of errors.)

---

[1]Leonard C. Labowitz and John S. Arents, "Physical Chemistry Problems and Solutions," Academic Press, 1969, p. 30.

PROBLEM 2-4: The heat of combustion of benzoic acid, measured in a bomb calorimeter, i.e., constant volume, was found to be -770.7 kcal/mole at 25°C. Find the heat of combustion of benzoic acid at 25°C in an open container, i.e., constant pressure, assuming complete condensation of water.

ANS: -771.0 kcal/mole

PROBLEM 2-5: (Labowitz & Arents, 1969, p. 20) The calorific value of food may be determined by measuring the heat produced by burning a weighed sample of food under constant volume conditions in a bomb calorimeter. The heat released by the total combustion of a 1.00 g (3.00×10^{-3} mole) sample of chicken fat under these conditions was found to be 10,000 calories at 37°C. Calculate the calorific value of the chicken fat in cal/gram at 37°C under constant pressure conditions. The reaction can be represented as follows:

$$C_{20}H_{32}O_2(s) + 27\ O_2(g) = 16\ H_2O(l) + 20\ CO_2(g).[1]$$
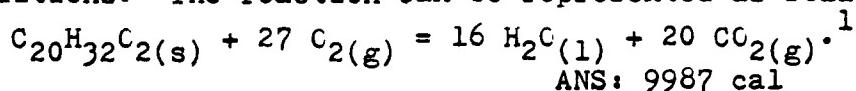
ANS: 9987 cal

PROBLEM 2-6: Using your data, how many significant figures are justified in the calculation of the heat of combustion, ΔH, of naphthalene (or unknown)? Show your reasoning, i.e., go through the calculations.

---

[1] Leonard C. Labowitz and John S Arents, "Physical Chemistry Problems and Solutions," Academic Press, 1969, p. 20.

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PRCBLEM 2-7: The first law of thermodynamics can be summarized in the following statements:

$$\Delta U = U_2 - U_1 = W \quad \text{(adiabatic)} \tag{1}$$

$$Q = \Delta U \quad \text{(no work)} \tag{2}$$

$$\Delta U = Q + W \tag{3}$$

$$\oint dU = 0 \tag{4}$$

where U is a function of the state of the system, and statement #4 is a statement of the conservation of energy. Show that statement #4 can be derived from statement #3. Hint: Consider a system that goes from state A to state B on one path and returns from state B to state A by another path.

PRCBLEM 2-8: When 450.74 mg of jet fuel were burned in a bomb calorimeter under a pressure of 25×10^5 Pa of O_2, (1 Pascal = 1 N-m^{-2}) the temperature change was found to be 1.7656 K. In order to produce the same temperature change in the calorimeter and products, it was necessary to operate a 10.000-Watt heater for 2061.9 seconds. A correction of 104.57 J was made for the energy liberated by the burning of the ignition wire. Calculate the value of ΔU per gram for the combustion of the fuel. (Rosenberg, R. M., "Principles of Physical Chemistry," Oxford University Press, New York, 1977, p. 319.)

ANS: -45.512 kJ/g

PRCBLEM 2-9: Using the value for ΔU of the fuel in PRCBLEM 2-9 with the formula C_8H_{18}, calculate ΔU and ΔH for the combustion of 1 mole of fuel. Assume ideal behavior. (Rosenberg, R.M., "Principles of Physical Chemistry," Cxford University Press, New York, 1977, p. 319.)

ANS: $\Delta U = -5199.0$ kJ/mol
$\Delta H = -5199 + .066$
$\Delta H \approx \Delta U$

ADIABATIC CALORIMETRY

Name _____ Date _____

M. DATA AND RESULTS	Benzoic Acid	Naphthlene
1. Temperature at firing t_1		
2. Correction factor for t_1 (if used)		
3. Corrected temperature (t_i)		
4. Final maximum temperature t_2		
5. Correction factor for t_2 (if used)		
6. Corrected temperature (t_f)		
7. cm of fuse wire initially		
8. cm of unburned fuse wire		
9. cm of fuse wire consumed		
10. Mass of sample and capsule		
11. Mass of metal capsule		
12. Mass of sample in grams		
13. Net temperature rise ($t_f - t_i$)		
14. Burette reading final		
15. Burette reading original		
16. mL Base used		
17. Normality of Base		
- -		
18. Correction in joules for burning of fuse wire		
19. Correction in joules for formation of HNO_3		
20. Heat capacity of calorimeter in joules/$^{\circ}$F		
21. Heat of combustion in joules/mole		
22. Maximum error in ΔH for Naphthalene		

Before leaving the laboratory, file with the instructor
(if required) a copy of the items above the dotted line.

APPENDIX D

CALORIMETRIC MEASUREMENTS OF HEATS OF NEUTRALIZATION

APPENDIX D

EXPERIMENT 3 - CALORIMETRIC MEASUREMENT OF HEATS OF
NEUTRALIZATION

A. STUDY GUIDE AND REVIEW ASSIGNMENT

1. Read section(s) on Heat of Solution in your lecture
textbook prior to lab. This should give you a short
overview of the theory necessary for this experiment.

2. Work the following which was taken from Metz (1976, p.43)

For the reaction between a strong acid and a strong
base, i.e., those that are essentially 100% ionized or
dissociated, the neutralization equation is essentially

$$H^+_{(aq)} + OH^-_{(aq)} = H_2O_{(1)}$$
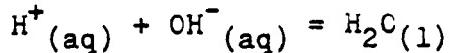
If the heats of formation at 25°C are -68.3171, 0 and
-54.957 kcal/mole for H_2O, H^+, and OH^-, respectively,
calculate the heat of neutralization for strong acids with
strong bases.

ANS: -13.360 kcal

3. Read the THEORY section and PROCEDURE section of this
experiment and complete this respective part of your report
prior to performing the experiment.

4. Supply definitions for the KEY WORDS. The majority of
these terms are discussed in the THEORY section and in your
lecture textbook. A more detailed explanation of these
terms can be found in the REFERENCES.

5. Complete the PRELIMINARY REPORT prior to class.

B. OBJECTIVES - You shall be able to:

1. Define and/or briefly discuss the KEY WORDS, including
any appropriate equations.

2. Summarize in writing how one determines heats of
neutralization.

3. Calculate ΔH_n for strong base with a strong acid, and
for a weak base with a strong acid.

C. KEY WORDS: (Supply equations where possible.)

Calorimetry

Differential heat of solution

Heat capacity, C

Heat of dilution

Heat of Ionization, ΔH_{ion}

Heat of Neutralization, ΔH_n

Hess's law

Integral heat of solution

Neutralization

D. PRELIMINARY REPORT - Answer the following questions prior to coming to the laboratory. You may be required to turn this sheet in for grading or you may have a quiz prior to performing the experiment.

1. What is the net ionic equation which occurs in the neutralization of a strong acid by a strong base?

2. How is the heat capacity related to the heat evolved and the temperature change (Give an equation)?

3. What is the relationship of Q_c to ΔH_c? Why?

4. How are Q_c, Q_e, ΔT_c, and ΔT_e related?

5. How will the base be introduced into the acid?

6. In this experiment you react 250 mL of 1.200 $\underline{N}$ HCl with 40.0 mL of 8.0 $\underline{N}$ NaOH. Which is in excess? Show the calculations.

7. What is the purpose of the ammeter readings in step 11 of the procedure?

E. REFERENCES

1. Crockford, H. D., et al., "Laboratory Manual of Physical Chemistry," John Wiley, New York, 1975, p. 116.

2. Metz, Clyde R., "Theory and Problems of Physical Chemistry," McGraw-Hill, New York, 1976, p. 43.

F. APPARATUS AND CHEMICALS

See your instructor for the following materials: Dewar vessel equipped with a stopper through which are inserted a sensitive thermometer, an insulated electrical heating element, a hand stirrer, and a metal tube with removable bottom; 250 ml volumetric flask; 1.00 $\underline{N}$ HCl; distilled water; 8.0 $\underline{N}$ NaOH; and 8.0 $\underline{N}$ NH_4OH.

G. PURPOSE

In this experiment you will determine the heat of neutralization of a strong acid with a weak base and together with the known value of ΔH_n for a strong acid-base reaction calculate the heat of ionization of the weak base.

H. THEORY

A study of your textbook and the references listed on the previous page shows that 57,200 joules (or 13,700 cal) are evolved when one mole of a strong base is neutralized by one mole of a strong acid in a dilute solution at $25°C$. The net ionic equation associated with this reaction is:

$$H^+ + OH^- = H_2O \qquad \Delta H_n = 57,200 \text{ J} \qquad (3-1)$$
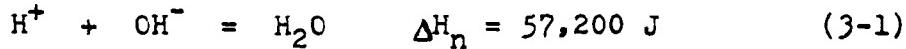
where we understand the symbol H^+ to mean the solvated hydrogen ion. For the strong acid-base reaction the increase in enthalpy, ΔH_n, is approximately the same regardless of which acid or base is used.

On the other hand, "when a dilute solution of a weak acid or base is neutralized, the heat of neutralization may be somewhat less because of the absorption of heat in the dissociation of the weak acid or base." (Daniels and Alberty 1975, p. 30)

The values of ΔH_n found in the literature are usually reported at $25°C$. Since ΔH is temperature dependent you should try to perform the experiment as close to $25°C$ as possible not only to be able to compare your results, but also because it will be easier to maintain at approximately room temperature.

As with all calorimetric experiments, we can determine the <u>heat capacity</u>, C, of the calorimetric system, i.e., the calorimeter and the solution. This is the amount of heat necessary to change the temperature of the system by $1°C$. In this experiment we will also determine the amount of heat generated by a heating device from the same initial to the same final temperature.

When the enthalpy change in a chemical reaction is measured by this calorimetric method, the temperature change in the calorimeter is compared with that produced by any known amount of heat generated electrically. In order that radiation, conduction, and similar thermal losses by the same in both cases, and in order that we may establish the mean heat capacity, C, of the system during the chemical process the electrical heating is carried out over a range of temperature similar to that observed during the chemical reaction.

This mean heat capacity, C, of the calorimeter and its contents is related to the amount of electrical heat, Q_e, and the temperature increase, ΔT_e, which is produced, by the relation

$$C = \frac{Q_e}{\Delta T_e},\tag{3-2}$$

where the units for Q_e are

$$Q_e = V(volts)I(amps)t(sec) = joules.\tag{3-3}$$

It should be noted that C depends not only on the value of ΔT, but on the actual initial and final temperature.

If we have been careful to conduct the electrical heating in accordance with the principles discussed above, the mean heat capacity, C, obtained from the electrical measurements will be related to the heat evolved during the chemical reaction and to the temperature change as follows

$$C = \frac{Q_c}{\Delta T_c}.\tag{3-4}$$

In this experiment the quantity Q_c is numerically equal to ΔH_c, but has the opposite sign

$$Q_c = -\Delta H_c.\tag{3-5}$$

This difference in sign is due to the fact that the change in enthalpy is that of the system while Q_c is the amount of heat gained by the surroundings.

The increase in enthalpy during any process is a function of temperature. Calorimetric measurements, which give us Q_c, involve a range of temperature. We are able to state the equality $Q_c = -\Delta H_c$ because the procedure to be followed is an adiabatic one. The calorimeter is so constructed and is operated so close to room temperature that the heat lost to or gained from the surroundings is small.

APPARATUS SETTINGS

1. Voltage 6.0 volts
2. Current 2.0 amps

DRAW SKETCH CF ELECTRICAL DIAGRAM HERE-----CHECK WITH INSTRUCTOR.
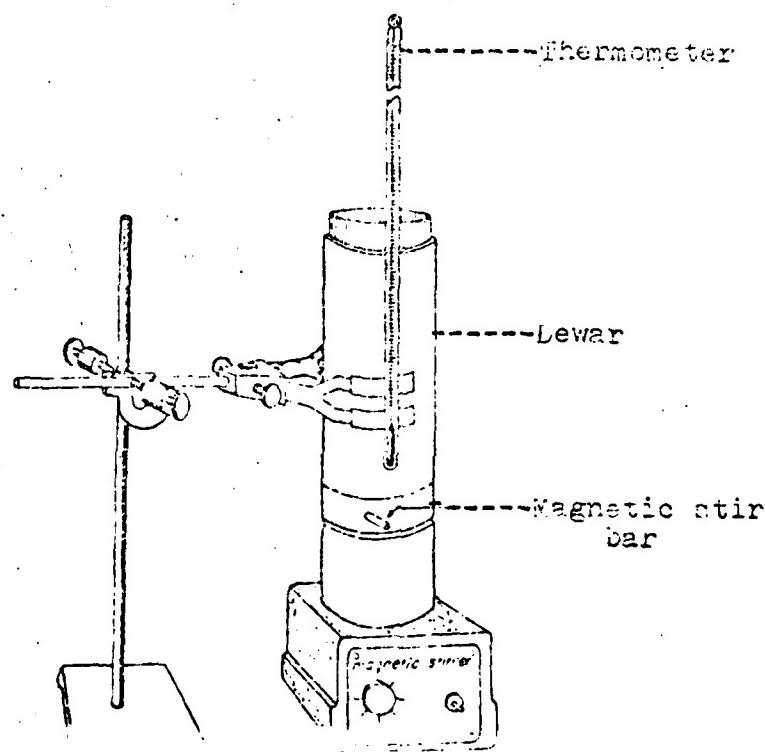
FIGURE 3-1: Calorimeter Assembly (Kamicha et al., 1979)

I. PRCCEDURE   (See FIGURE 3-1)

1. Check out the special apparatus for Experiment 3. The apparatus consists of a Dewar vessel equipped with a stopper through which are inserted a sensitive (and expensive) thermometer, an insulated electrical heating element, a hand stirrer, and a metal tube with removable bottom.

2. Familiarize yourself with the operation of the stirrer; adjust the cork so that the stirrer can be moved freely. The removable bottom, a rubber stopper, of the metal tube must be pushed out easily, and yet it must not leak before that time. By practice, decide how tightly to place the stopper in the bottom of the tube; it should be seated firmly with a twisting motion, but should not be forced hard into the tube.

3. Fill the 250-mL volumetric flask just to the mark with 1.2000 $\underline{N}$ HCl solution from the stock bottle. Cool this flask to about 4°C below room temperature and then empty all the acid into the clean Dewar vessel. Fill the 250-mL volumetric flask with distilled water and cool to the same temperature. Use part of the distilled water to rinse the acid out of the flask into the Dewar, and pour the remainder directly into the Dewar. Alternatively, you can cool the 500-mL of water prior to this step and then use this cool water to make the solutions.

4. Put 40 mL of 8.0 $\underline{N}$ NaOH (a slight excess) into the metal tube and assemble the apparatus in the Dewar vessel. Stir gently, (Dewar vessels are thin) and continuously, until the thermometer shows a constant temperature. Record this temperature. Tap the thermometer lightly before reading.

5. Now carefully push the stopper out of the metal tube and immediately resume regular stirring. Record the temperature at set 15 second intervals until a constant (or slowly falling) temperature is reached. Record the maximum temperature attained. You will use this data to plot a graph of temperature versus time and for calculating ΔT_c.

6. Raise the stopper from the Dewar flask; allowing any solution adhering to the apparatus to drain back into the flask. Set the stopper and apparatus in a ring support stand.

7. Test the solution in the flask with indicator paper to be sure that excess base was added.

8. Fill the metal tube with crushed ice and stir the solution in the Dewar to cool it to approximately the initial temperature. In this case make certain that the stopper in the metal tube is securely seated in the tube so

that neither ice nor ice water leaks from the metal tube into the Dewar.

9. Discard the ice and ice water in the metal tube, and replace the stopper assembly in the Dewar. Stir and read the thermometer at regular intervals until a constant reading is obtained.

10. Connect the heater coil to the binding posts of the electrical unit. Record the starting temperature and the starting time to the closest second. Turn the toggle switch on.

11. Stir continually, take ammeter readings every 30 seconds, and observe the thermometer. When the temperature has reached a value about half a degree lower than that reached for the reaction, take a final ammeter reading, note the time, and turn the toggle switch off.

12. Continue to stir and to observe the thermometer until a constant or slowly falling temperature is reached. Record the maximum reading. It is not essential that the rise in temperature in this part of the experiment, be identical with that in the first part of the experiment, but only approximately the same.
NOTE: In the case of failure in the first attempt at electrical heating, this part of the experiment may be repeated without performing the neutralization again. Two or three voltmeter readings (at a definite ammeter reading) are sufficient to determine the voltage drop across the heating coil (while hot). Thus, the same voltmeter may be used by several pairs of students.

13. Repeat steps 3 through 12, but use an ammonium hydroxide solution instead of sodium hydroxide.

J. CALCULATIONS

1. Plot temperature versus time for both chemical reaction determinations. Lay a straightedge along the points obtained after the temperature change becomes constant and extrapolate the line back to zero time. Determine ΔT, as of zero time, from this plot. Compare this with the simple difference between the temperature at zero time and the maximum temperature reached. Report the two values and explain why a difference appears.

2. Show the calculations for both NaOH and NH_4OH for steps 14, 15, 16, and 17; on the DATA AND RESULTS sheet.

3. Perform a maximum error analysis treatment as outlined in the UNIT on the treatment of errors.

4.   Include the solutions and the answers to the assigned
PRCBLEMS at the end of your lab report.

5.   Write a computer program for this experiment and include
the program and run.

K.   EXAMPLES AND PRCBLEMS

EXAMPLE 3-1:   (Metz, 1976, p. 43)   Consider the titration of
a weak acid, such as HCN, with a strong base, such as NaCH:

$$HCN_{(aq)} + NaCH_{(aq)} = NaCN_{(aq)} + H_2C_{(1)}.$$

If the standard heats of formation are -68.3174, -21.2,
-112.236 and 25.2 kcal/mole at 25°C for H_2C, NaCN, NaCH, and
HCN, respectively, calculate $\Delta H^{\circ}_{298(Neutralization)}$.
Account for thedifference from -55.898 kJ/mole as found for
the strong acid-strong base case.

Using Hess's law

$$\Delta H^{\circ}_{Reaction} = \Delta H^{\circ}_{f\text{-}Products} - \Delta H^{\circ}_{f\text{-}Reactants} = \Delta H^{\circ}_{N}$$

$$\Delta H^{\circ}_{N} = (-68.3174 + (-21.2)) - (-112.236 + 25.2)$$

$$= (-2.5\ kcal)(4.184\ kJ/kcal) = \underline{-10.5\ kJ}.$$

Because HCN is a weak acid, the titration reaction may be
considered to be the sum of two steps:

$$HCN_{(aq)} = H^{+}_{(aq)} + CN^{-}_{(aq)} \qquad\qquad \Delta H^{\circ}_{Ionization}$$

$$H^{+}_{(aq)} + CN^{-}_{(aq)} + NaCH_{(aq)} = NaCN_{(aq)} + H_2C_{(1)}, \Delta H^{\circ}_{N} = -55.898$$

where the ionization process required
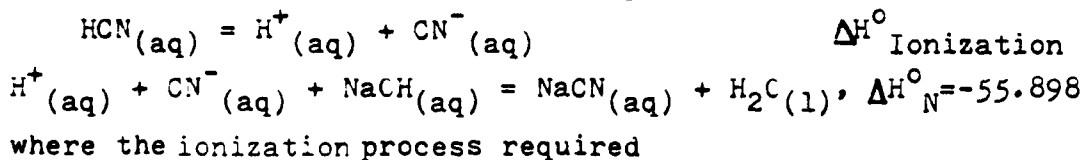
$$\Delta H^{\circ}_{Ionization} = (-10.5) - (-55.898) = \underline{45.4\ kJ}$$

EXAMPLE 3-2:   (Metz, 1976, p. 43)   The heat of reaction for
diluting one mole of solute in a solution of given
concentration, by adding solvent to produce a solution of
different concentration, is known as the Heat of Dilution.

    What is $\Delta H^{\circ}_{Dilution}$ for diluting a solution
containing one mole of $AgNC_3$ in 100 moles of matter by adding
400 moles of water?   The heats of formation are -24.637 and
-24.362 kcal/mole for the solutions consisting of 100 and
500 moles of water, respectively, added to one mole of
$AgNC_3$ at 25°C.

Again using Hess's law

$$\Delta H^o_{Dilution} = \Delta H^o_{298}(\text{solution, AgNC}_3 \text{ in } 500 \text{ H}_2\text{C}) -$$

$$\Delta H^o_{298}(\text{solution, AgNC}_3 \text{ in } 100 \text{ H}_2\text{C})$$

$$= (-24.362) - (-24.637) = 275 \text{ cal}$$

$$= \underline{1.15 \text{ kJ}}$$

PROBLEM 3-1: Why should the temperature of the contents of the calorimeter be close to that of the laboratory?

PROBLEM 3-2: Discuss the errors involved in estimating the heat capacity of the calorimeter, and suggest how this quantity could be obtained more precisely. Assess the overall accuracy of the determinations and give the values of the enthalpy changes to the appropriate number of significant figures.

PROBLEM 3-3: When the heat of ionization of a weak base is calculated from two heat of neutralization measurements, as in this experiment, what assumptions are made as to the ionization of strong acids, strong bases, and salts such as NaCl?

PROBLEM 3-4: How will the heat of neutralization depend
on the concentration of a strong acid reacting with a
strong base?

PROBLEM 3-5: How would the heat of neutralization of
(a) nitric acid and (b) sulfuric acid with sodium hydroxide
compare with the result obtained for hydrochloric acid?

PROBLEM 3-6: (Metz, 1976, p. 55) Calculate $\Delta H^{o}_{f\,298(Neutral)}$
for the reaction between $HCl_{(aq)}$ and $NaOH_{(aq)}$ if
the heats of formation are -40.023, -112.236, -97.302, and
-68.3174 kcal/mole at $25^{o}C$ for HCl, NaOH, NaCl, and H_2O,
respectively, in very dilute solutions.

ANS: -55.898 kJ

HEAT OF NEUTRALIZATION

Name_____Date_____

L.	DATA AND RESULTS	NaOH	NH$_4$OH
1.	Normality of acid	_____	_____
2.	Moles of acid neutralized	_____	_____
3.	Initial temperature (chemical process)	_____	_____
4.	Final temperature (chemical process)	_____	_____
5.	Temperature rise during neutralization	_____	_____
6.	Initial temperature (electrical heating)	_____	_____
7.	Final temperature (electrical heating)	_____	_____
8.	Temperature rise during electrical heating	_____	_____
9.	Total time of heating, seconds	_____	_____
10.	Voltage drop across heater while hot	_____	_____
11.	Average amperes	_____	_____
12.	Maximum deviation of current from average during run	_____	_____
13.	Apparatus number	_____	

14.	Electrical energy input, joules	_____	_____
15.	Heat evolved by neutralization, joules	_____	_____
16.	Molal heat of neutralization (enthalpy increase)	_____	
17.	Molal heat of ionization (enthalpy increase)		_____

Before leaving the laboratory, file with the instructor a
copy of the items above the dotted line.

APPENDIX E

CHEMICAL EQUILIBRIUM

APPENDIX E

EXPERIMENT 4 - CHEMICAL EQUILIBRIUM

A. STUDY GUIDE AND REVIEW ASSIGNMENT

1. Read sections on Chemical Equilibrium in your lecture textbook prior to lab. This should give you a short overview of the theory necessary for this experiment.

2. Work the following problems taken from Daniels and Alberty (1975, p. 181):

A. At $55^{\circ}C$ and 1 atm the average molecular weight of partially dissociated N_2O_4 is 61.2 g/mole. Calculate (a) α and (b) K_p for the reaction $N_2O_{4(g)} = 2NO_{2(g)}$. (c) Calculate α at $55^{\circ}C$ if the total pressure is reduced to 0.1 atm.

ANS: (a) 0.503, (b) 1.36, (c) 0.876.

B. For the reaction $N_2O_{4(g)} = 2NO_{2(g)}$, K_p at $25^{\circ}C$ is 0.141. What pressure would be expected if 1 g of liquid N_2O_4 were allowed to evaporate into a liter vessel at this temperature? Assume that N_2O_4 and NO_2 are ideal gases.

ANS: 0.351 atm.

3. Read the THEORY section and the PROCEDURE section of this experiment and complete this respective part of your report prior to performing the experiment.

4. Supply definitions for the KEY WORDS. The majority of these terms are discussed in the THEORY section and in your lecture textbook. A more detailed explanation of these terms can be found in the REFERENCES.

5. Complete the PRELIMINARY REPORT prior to class.

B. OBJECTIVES - You shall be able to:

1. Define and/or briefly discuss the KEY WORDS, including any appropriate equations.

2. Summarize in writing how one determines K_p in a general equilibrium reaction.

3. Calculate values for ΔH°, ΔG°, and ΔS° from your equilibrium data.

4. Derive Equation 4-8 and explain its significance.

5. Write a computer program to calculate the results required in the DATA AND RESULTS section. Include a least squares calculation for ΔH^0 in your program.

6. Use the results obtained in this experiment to draw a graph of $\ln K_p$ versus $1/T$.

NOTE: You should use your raw data, i.e., manometer readings and temperature readings and have the computer do all the calculations. Then you should take the computer calculated values of $\ln K_p$ and $1/T$ and make a plot of $\ln K_p$ versus $1/T$ and compare your eyeball value of ΔH with the least squares value from your program.

C. KEY WORDS: (Supply equations where possible.)

Activity

Dalton's law

Enthalpy of Reaction, ΔH

Equilibrium

Equilibrium constant, K_c

Equilibrium constant, K_p

Gibbs Free energy, ΔG

Partial pressure

D. PRELIMINARY REPORT - Answer the following questions
prior to coming to the laboratory. You may be required to
turn this sheet in for grading or you may have a quiz prior
to performing the experiment.

1. List two cautions in this experiment.

2. How do you determine the weight of N_2O_4 for this
experiment?

3. How do you know when the pressure correctly corresponds
to the temperature?

4. What is the objective of plotting $\ln K_p$ versus $1/T$
in this experiment?

5. Write an equilibrium expression, K_p, for the system
being studied in this experiment, in terms of concentration
of reactants and products.

E. REFERENCES

1. Daniels, F., R. A. Alberty, "Physical Chemistry," John Wiley & Sons, Inc., 1975, pp. 149-181.

2. Daniels, et al., "Experimental Physical Chemistry," McGraw-Hill, New York, 1970, pp.102-106.

3. Metz, Clyde R., "Theory and Problems of Physical Chemistry," McGraw-Hill, New York, 1976, pp. 78-94.

F. APPARATUS AND CHEMICALS

See your instructor for directions on operating the apparatus, a sketch of which is shown in Figure 4-1.

(See J. Chem. Educ., 12, p. 318--21, 1935)

Stopcock #2

Mercury Reservoir, R

Manometer

Stopcock #1

Reaction tube, T

Gauge, G

Sink

Pointer, P

Reference pointer, P'

Tubing
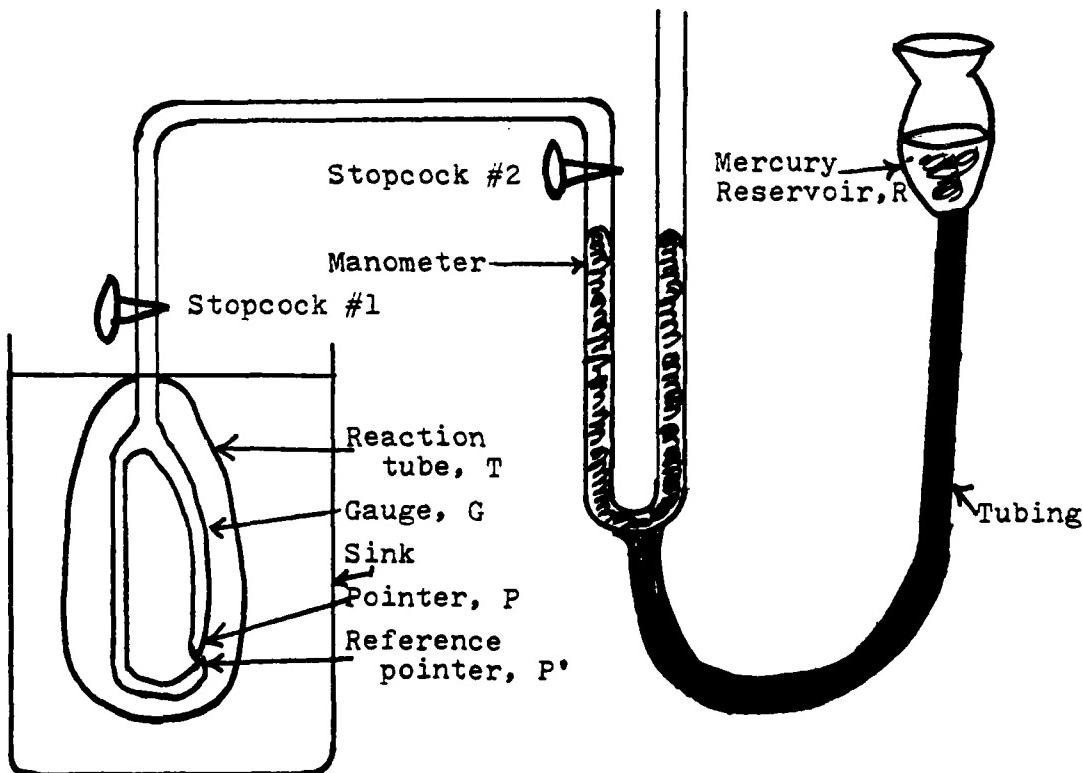
Figure 4-1: Apparatus

The reaction tube T has been filled with a known weight of N_2C_4 and sealed. The pressure of the equilibrium mixture is measured with the sensitive gauge G, which is made of very thin-walled glass. When the pressure inside the gauge differs from the pressure outside the gauge, the pointer P is out of alignment with the reference pointer, P'. The pointer is brought back into line by raising or lowering the mercury reservoir R; the pressure inside the reaction tube is determined by adding the difference in the two mercury levels in the manometer to the atmospheric pressure.

CAUTION: The gauge is a very delicate instrument. BE SURE THAT YOU UNDERSTAND THE OPERATION OF THE GAUGE AND MERCURY MANOMETER BEFORE YOU TOUCH THE APPARATUS. The thin glass membrane of the gauge is very fragile, and will be broken if it sustains too great a pressure difference. In addition the gas contained in the apparatus, N_2C_4, is corrosive and very poisonous.

G. PURPOSE

One purpose of this experiment is to determine the values of the equilibrium constant over a selected range of temperatures for the gaseous reaction

$$N_2C_4 = 2NC_2.$$

This data is used to calculate the approximate value of the enthalpy of reaction, ΔH^0.

H. THEORY

Assuming the activities of nitrogen tetroxide and nitrogen dioxide to be equal to their partial pressures, the following general relationship applies to any equilibrium mixture of these two gases at a given temperature

$$\Delta G^0 = -RT \ln K_p = -RT \ln \frac{(P_{NC_2})^2_{eq}}{(P_{N_2C_4})_{eq}} \qquad (4-1)$$

wher K_p is the equilibrium constant for the dissociation of nitrogen tetroxide at temperature T.

Since it is rather difficult to determine the equilibrium partial pressures of N_2C_4 and NC_2 directly, a procedure using the degree of dissociation of the N_2C_4 will be used. Let us consider a situation in which n_0 moles of pure N_2C_4 are put into a vessel of volume V at temperature T degrees Kelvin. The N_2C_4 will dissociate into NC_2 until equilibrium is established.

Let the degree of dissociation at the point of equilibrium be represented by q and the total pressure by P_t. Then from the following outline you can see that since q is the degree of dissociation, qn_o is the number of moles dissociating. The mole ratio is 1 to 2, thus for qn_o moles of N_2O_4 dissociating, $2qn_o$ moles of NO_2 will be formed. The number of moles of N_2O_4 left is then (n_o-qn_o) or $n_o(1-q)$. The total moles of both gases at equilibrium is just the sum of the number of moles of the two individual gases, which equals $n_o(1-q) + 2n_oq = n_o(1+q)$.

	N_2O_4	$2NO_2$
Initial moles	n_o	0
Change to produce equilibrium	$-n_oq$	$+2n_oq$
Equilibrium moles	$n_o(1-q)$	$2n_oq$

Total moles at equilibrium $= n_o(1-q) + 2n_oq = n_o(1+q)$

By Dalton's law, the partial pressure, P_x, of each gas is equal to its mole fraction, N_x, multiplied by the total pressure, P_t,

$$P_x = N_xP_t \tag{4-2}$$

On this basis

$$P_{NO_2} = \frac{2qn_o}{n_o(1+q)}P_t = \frac{2q}{(1+q)}P_t \tag{4-3}$$

$$P_{N_2O_4} = \frac{n_o(1-q)}{n_o(1+q)}P_t = \frac{(1-q)}{(1+q)}P_t \tag{4-4}$$

therefore,

$$K_p = \frac{(P_{NO_2})^2}{(P_{N_2O_4})} = \frac{4q^2P_t}{1-q^2} \tag{4-5}$$

Assuming ideal gas conditions, if we know q and P_t we can calculate the value of K_p. In this experiment P_t is measured directly, but q must be obtained indirectly from known or measured values of other quantities. At equilibrium,

$P_tV = n_tRT$; but $n_t = n_o(1+q)$, thus, $P_tV = n_o(1+q)RT$.

For this calculation we know n_o, since the weight of N_2O_4 is given for each apparatus. The volume of the reaction tube, V, is given, P_t and T are measured, and R is the gas constant whose value is known. Therefore, we can calculate

q, as seen below, where if M is the molecular weight of N_2C_4,

$$P_tV = n_o(1+q)RT, \quad P_tV = (w/M)(1+q)RT, \quad q = \frac{(P_tVM)}{wRT} - 1. \quad (4-6)$$

The next equation relates the equilibrium constant to temperature

$$d(\ln K_p) = \frac{\Delta H^o}{RT^2} dT \qquad (4-7)$$

If ΔH^o is assumed to be constant over the given temperature range, then upon integration we can write

$$\ln K_p = -\frac{\Delta H^o}{RT} + \text{Constant} \qquad (4-8)$$

and a plot of K_p versus $1/T$ is a straight line, and ΔH^o may be calculated from the slope of the line(See PROBLEM 4-1).

I. PROCEDURE

1. Record on the data sheet the weight of N_2C_4 and the volume of the reaction tube. These figures are scratched on the side of the tube.

2. If it is not already opened, open stopcock #2 at the upper end of the manometer.

3. Keep the open end of the manometer covered to protect the mercury from dust.

4. Make sure stopcock #1 just above the reaction vessel is open, then raise and lower the mercury reservoir slightly while observing the effect upon the pointer P.

5. Take the first reading at room temperature. Align the pointers, record the height of the mercury in both arms of the manometer, and then record the temperature of the water bath.

6. Slowly heat the water bath and repeat the alignment of the pointers at several different temperatures up to approximately 40^oC (a total of five readings). (Each partner should perform some of the alignments.)

7. REMEMBER YOU MUST MOVE THE MERCURY RESERVOIR TO COMPENSATE FOR ANY CHANGE IN THE TEMPERATURE OF THE BATH.

8. When you have finished taking the readings, cool the water in the bath slowly (15-20 minutes) while one student watches the pointer and instructs the other student in the movement of the mercury reservoir.

9. Close stopcock #1 just above the reaction vessel. Close stopcock #2 at the top of manometer. Pressure inside the reaction tube should now be back to that at room temperature.

J. CALCULATIONS (NOTE: In using the equations given in this experiment for making your calculations, the pressure should be in atmospheres.)

1. Calculate the degree of dissociation, q, at each temperature using equation 4-6.

2. Calculate the equilibrium constant, K_p, at each temperature using equation 4-5.

3. Find the standard free energy change at each temperature using equation 4-1.

4. Plot ln K_p, as ordinate, versus 1/T. This is a plot of equation 4-8. The value of ΔH° can then be determined from the slope of the line, which is calculated by the method of least squares. Include the graph at the end of your report.

5. You should do all the calculations by means of a computer program including a least squares determination of ΔH°.

6. Perform a maximum error analysis treatment as outlined in the UNIT on treatment of errors for q and K_p assuming logical values for the errors in w, T, P_t, and P_v.

7. Include the solutions and the answers to the PROBLEMS assigned by your instructor at the end of your report.

K. EXAMPLES AND PROBLEMS

EXAMPLE 4-1: Another method used to calculate the degree of dissociation, q, is from the knowledge of the average molecular weight of the gases involved, or the apparent molecular weight. In this case

$$q = \frac{M_1 - M_2}{M_2}$$

where M_1 is the molecular weight of the undissociated gas, and M_2 is the average weight of the gases when the gas is partially dissociated.

If 1.588 g of nitrogen tetroxide gives a total pressure of 760 Torr when partially dissociated in a 500-cm^3 glass vessel at 25°, what is the degree of dissociation q? What is the value of K_p? What is the degree of dissociation at a total pressure of 0.5 atm and the same temperature? (Daniels and Alberty, 1975, p. 162)

$$M_2 = \frac{RTg}{PV}$$

$$= \frac{(0.08205 \text{ liter-atm/mole-K})(298.1 \text{ K})(1.588 \text{ g})}{(1 \text{ atm})(0.500 \text{ liter})}$$

$$= 77.68 \text{ g/mole}$$

$$q = \frac{92.02 - 77.68}{77.68} = 0.1846$$

$$K_p = \frac{4q^2 P}{1-q^2} = \frac{(4)(0.1846)^2(1)}{1 - (0.1846)^2} = 0.141$$

The degree of dissociation at 0.5 atm is obtained as follows:

$$K_p = 0.141 = \frac{4q^2(0.5)}{1-q^2}$$

$$2q^2 = 0.141(1 - q^2)$$

$$\underline{q = 0.257}$$

EXAMPLE 4-2: (Daniels and Alberty, 1975, p. 170) Calculate the change in Gibbs free energy, ΔG, for the production of $2NO_2(g)$ at 1 atm from $N_2O_4(g)$ at 10 atm at 25°C. As may be calculated from the data in EXAMPLE 4-1, the standard Gibbs free energy for the reaction $N_2O_4 = 2NO_2$ is +1161 cal, so that this reaction is not spontaneous at 25°C, Equation 4-1 becomes

$$\Delta G = \Delta G^o + RT \ln \frac{(P_{NO_2})^2}{(P_{N_2O_4})}$$

$$= +1161 + (1.987)(298) \ln \frac{1^2}{10}$$

$$= \underline{-212 \text{ cal}}$$

Thus the production of $NO_2(g)$ at 1 atm from $N_2O_4(g)$ at 10 atm is a spontaneous process. Thus a continuous process would be thermodynamically feasible if N_2O_4 was maintained at

10 atm and NC_2 was withdrawn by some method so that its partial pressure was maintained at 1 atm.

PROBLEM 4-1: How can you tell if ΔH^o depends on the temperature?

PROBLEM 4-2: How can you calculate the entropy change, ΔS^o, in this experiment? Is ΔS^o a function of temperature? Calculate a value for ΔS^o at $25^o C$ using your data.

PROBLEM 4-3: Calculate K_p at $80^o C$ using your data.

PROBLEM 4-4: By use of EXAMPLE 4-1, calculate q and K_p for the reaction $N_2C_4 = 2NC_2$ if at $55^o C$ and 1 atm the average molecular weight of partially dissociated N_2C_4 is 61.2 g/mole.

CHEMICAL EQUILIBRIUM

Name_____Date_____

L. DATA AND RESULTS

1. Weight, w, of N_2C_4_____
2. Volume, V, of the reaction tube_____
3. Molecular weight, M, of N_2C_4_____
4. Value of R to be used_____
5. Moles of N_2C_4, n_o_____

No. of run	1	2	3	4	5
6. Manometer (outside)					
(inside)					
7. Barometer Reading					
8. P_t (mm Hg)					
9. a. $t\,^oC$					
b. T K					
10. 1/T					
11. Degree of Dissociation, q					
12. $\ln K_p$					
K_p					
13. ΔG					

14. ΔH = _____

NCTE: Items 8, 9b - 14 should be included in your program
and are not necessary above.

If required by the instructor then before leaving the
laboratory, file with the instructor a copy of the items
above the dotted line.

APPENDIX F

ELECTROCHEMISTRY UNIT

APPENDIX F

ELECTROCHEMISTRY

EXPERIMENT 5:   PREPARATION OF A CALOMEL HALF-CELL

A.   STUDY GUIDE AND REVIEW ASSIGNMENT

1.   Read the Electromotive Force (Electrochemical concepts)
chapter to obtain an overview of the material as contained
in your lecture textbook.

2.   Using the examples in your text and the examples at the
end of Experiments 6 and 7 of this UNIT, solve the problems
at the end of this experiment.

3.   Be prepared to discuss the problems at the end of
Experiment 5 at the start of the laboratory period.

4.   Read the PROCEDURE SECTION of Experiment 5 prior to
coming to class.

5.   Supply definitions for the KEY WORDS. The majority of
these terms are discussed in your textbook.

6.   Be prepared to discuss the following items at the start
of the laboratory period. These items are NOT directly
related to the experiments you will be performing, BUT they
are necessary in understanding the concepts that are
presented in this UNIT.
   a.   Faraday's laws
   b.   Equivalent weights
   c.   Balancing redox equations
   d.   Electromotive series and standard reduction potentials
   e.   The term "Operational Definition"

B.   OBJECTIVES - You shall be able to:

1.   Define and/or briefly discuss the KEY WORDS.

2.   State Faraday's laws in words.

3.   Apply Faraday's laws in solving problems at the end
of this experiment.

4.   Build a calomel half-cell.

5.   LEARN PHYSICAL CHEMISTRY CONCEPTS related to electro-
chemistry in the laboratory with little or no reinforcement
in the lecture portion of the course.

The last objective is especially important since you will have little or no contact with the concepts introduced in this UNIT in the lecture part of the course. You must, therefore, correlate your reading assignments to your laboratory work in a self-learning type of approach. You must likewise take sole responsibility to familiarize yourself with the KEY WORDS since they will not be introduced in lecture.

C. KEY WORDS: Supply operational definitions

Calomel

Calomel elcetrode

Decinormal

Electrochemistry

Electrodes

Electrolytes

Equivalent

Half-reaction

Reference electrodes

Salt bridge

D. REFERENCES - See the chapter or experiments on electro-chemistry in your lecture textbook, or other books of your choosing.

1. Daniels, F., and R. A. Alberty, "Physical Chemistry," John Wiley, New York, 1975, pp. 191-214.

2. Daniels, et al., "Experimental Physical Chemistry," McGraw-Hill, New York, 1970, pp. 178-201.

3. Metz, C. R., "Theory and Problems of Physical Chemistry," McGraw-Hill, New York, 1976, pp. 130-143.

4. Shoemaker, D. P., and C. W. Garland, "Experiments in Physical Chemistry," McGraw-Hill, New York, 1962, pp. 185-213.

******* THERE IS NO LABORATORY REPORT FOR EXPERIMENT 5!*****

E. APPARATUS AND CHEMICALS

Calomel half-cell vessels, Hg; Hg_2Cl_2; agar; 0.100 $\underline{N}$ KCl;
platinum-point electrodes. Acetone and concentrated
HNO_3-HCl mixture. For student work or potentiometric
titrations where only changes in the emf are to be recorded,
ordinary mercury C.P. salts may be used with reasonable
success.

F. INTRODUCTION

Electrochemistry is the science of chemical
reactions caused by an electric current, and of reactions
that lead to the development of electrical energy. Many
scientists regard electrochemistry as a specialized branch
of physical chemistry.
Electrochemistry began toward the end of the
eighteenth century with the work of the Italian anatomist
Luigi Galvani in his famous experiments on frogs. Develop-
ment of electrochemistry continued through the experiments
of the eighteeth-century Italian physicist Alessandro Volta,
and was culminated through the efforts of an international
array of scientists: The Swedish chemist Svante Arrhenius,
the German physical chemist Walter Nernst, the Dutch physical
chemist Jocobus Van't Hoff, and the Russian-German physical
chemist Friedrich Ostwald.
Many of the thermodynamic relationships associated
with chemical reactions came about through a study of
electrochemistry. This was especially due to the fact that
the amount of electrical energy produced or consumed during
electrochemical changes could be measured much more
accurately than many other properties. Today scientists
use cell potentials to determine any of the following:
1. Free energy of reaction,
2. Entropy and enthalpy of reaction as a function of temp.,
3. Activities and activity coefficients,
4. Equilibrium constants,
5. Solubility products or dissociation constant.
Many electrochemical processes are important in
science and industry. For example, hydrogen, oxygen, ozone,
hydrogen peroxide, chlorine, sodium hydroxide, and oxygen
compounds of the halogens are produced by electrochemical
processes. Other applications include refining of metal,
electroplating of metals and the production of metals. Thus
electrochemistry is an important topic in a course in
physical chemistry, and you should ask yourself: (1) How
can I apply these concepts to what I have already learned in
physical chemistry, and (2) How does electrochemistry form a
part of thermodynamics?

G. EXPERIMENTAL PROCEDURE

A <u>half-cell</u> which has been widely used in physico-chemical (Cf or pertaining to the physical and chemical properties of matter) is the <u>Decinormal Calomel</u> Half-Cell. It usually consists of successive layers of mercury, mercury-calomel paste, and 0.1000 <u>N</u> KCl solution. A platinum wire is used to effect electrical contact with the pool of mercury. The physical form of the cell can be made such that the KCl solution serves as a salt-bridge as well as the required electrolyte for the electrode reaction. A typical electrode is shown in Figure 5-1 but is not necessarily like the one you will make. Draw a picture of your calomel cell as part of your laboratory report for Experiment 6.

1. Mercury can be an extremely toxic substance. Mercury poisoning may result from inhalation of mercury vapor or the dust of mercury salts. Mercury in a suitable medium can be absorbed through the unbroken skin. Also mercury poisoning is cumulative, i.e., it is accumulated by the body. Therefore, be cautious when handling the metal so that spills do <u>not</u> occur. ADVISE YOUR INSTRUCTOR IMMEDIATELY IF YOU SPILL EVEN A MINUTE AMOUNT.

2. You will be using electrode vessels that have been used before. They may still contain mercury. You will be instructed to save as much mercury as possible for recycling. After the electrode vessel has been emptied, clean with concentrated HNO_3-hCl mixture. Then rinse the vessel several times with small portions of distilled water. Invert the electrode vessel and allow to drain for several minutes. Complete the drying process with acetone rinses. Finally dry the vessel with a gentle stream of air.

3. Lightly grease the stopcock with a very small amount of lubricant being careful that a grease plug does not form in one of the holes in the stopcock. Fill the side-arm with mercury; take care that no air bubbles are left between the mercury and the platinum contact wire. Perform the operation over a bucket or some other container so that any mercury that drops will be caught by the container.

4. Fill the bulb of the electrode vessel with mercury. Calomel must not be permitted to come in contact with platinum wire; if the bulb is filled completely with mercury it is difficult for particles of calomel to work down to the platinum. (The mercury used in the cell itself must be especially pure.)

FIGURE 5-1: The

Calomel Electrode

(Barrow, G. M.,
"Physical Chemistry,"
McGraw-Hill, New York,
1966, p. 718.)
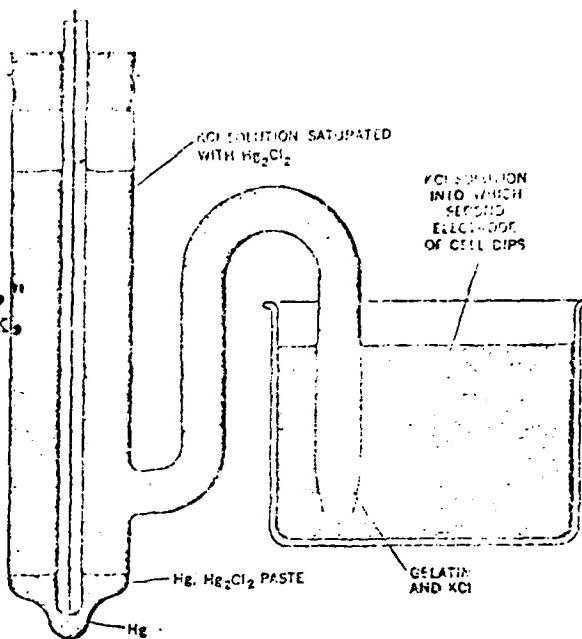
5. Fill the vessel, including reservoir and connecting arm,
with 0.100 N KCl solution which has been equilibrated with
mercury-calomel paste again being careful that no air
bubbles form in any portion of the solution.

6. Cover the mercury with a layer of mercury-calomel paste
at least 1 cm thick; use a dropping-pipette to effect the
transfer, and avoid splattering of the paste by keeping the
tip of the pipette just a little above the surface of the
mercury while discharging paste.

7. Label your cell and see instructor for storing it in a
safe place.

        When the cell is in use, the 3-way stopcock is
turned so that the main bulb and connecting arm are joined;
the KCl reservoir is isolated. Care must be taken so that
KCl solution does not siphon out of the electrode vessel.
Care must be exercised to prevent contaminant liquids from
being sucked back into the connecting arm; occasional
flushing of this arm with solution from the reservoir will
remove any contaminant which may have diffused into the arm.

NO LABORATORY REPORT IS REQUIRED FOR THIS EXPERIMENT.

H. PROBLEMS

PROBLEMS 5-1: Write the half-cell notation for the reaction of $Br_2(l)$ to form Br^- on a platinum electrode. Also, find E^O for the half-cell.

PROBLEM 5-2: Write the cell notation and find E^O for the reaction

$$Mg_{(s)} + Pb^{2+}_{(a=1)} = Mg^{2+}_{(a=1)} + Pb_{(s)}$$
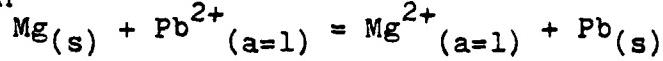
PROBLEM 5-3: A reaction proceeds as written (assuming all concentrations are unity) when E^O is _____.

PROBLEM 5-4: What is the expression of the equilibrium constant for the following reaction?

$$2Cr_{(s)} + 3Cu^{2+} = 2Cr^{3+} + 3Cu_{(s)}$$
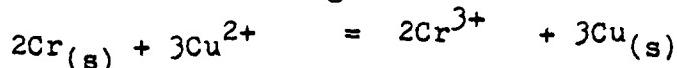
PROBLEM 5-5: The same quantity of electricity was passed through two separate electrolytic cells containing solutions of copper sulfate ($CuSO_4$) and silver nitrate ($AgNO_3$), respectively. The reactions at the cathodes in the two cells are

First cell: $Cu^{2+} + 2e^- \longrightarrow Cu_{(s)}$

Second cell: $Ag^+ + e^- \longrightarrow Ag_{(s)}$
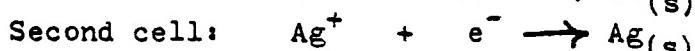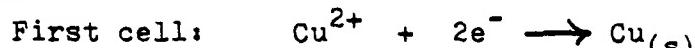
If 3.18 grams of Cu were deposited in the first cell, how many grams of Ag were deposited in the second cell?

PROBLEM 5-6: In the reduction of MnO_4^- to Mn^{2+}, the gram equivalent weight of MnO_4^- is _____ times its gram formula weight.

EXPERIMENT 6: CALIBRATION OF CALOMEL ELECTRODE

A. STUDY GUIDE AND REVIEW ASSIGNMENT

1. Read the THEORY section.

2. Be prepared to discuss the Nernst equation and thermo-
dynamic relationships related to electrochemical calcula-
tions at the start of the laboratory period.

3. Read the PROCEDURE section prior to performing the
experiment.

4. Complete the PRELIMINARY REPORT prior to the laboratory.
The purpose of this report is to prepare you to perform the
experiment. You should be prepared to answer the questions
as part of a closed book quiz.

5. Using your calomel half-cell, a hydrogen electrode, and
a potentiometer, determine the electromotive force of your
half-cell, as well as other thermodynamic values indicated
in PROBLEM 6-4.

B. OBJECTIVES - You shall be able to:

1. Define and/or briefly discuss the KEY WORDS.

2. Correctly diagram a cell reaction, label important
components, and describe the operation of the cell in words.

3. Represent an electrochemical cell in the conventional
way, write the two half-reactions and the overall cell
reaction, calculate the standard voltage of the cell from
standard reduction potentials, and determine whether or not
the cell reaction is a spontaneous one, e.g., see
PROBLEM 6-3.

C. KEY WORDS: (Supply operational definitions)
Activities
Anode
Cathode
Conductor
Coulomb
Current
E, Electrochemical potential (volts)

Electrochemical cells

Electrolysis

Electromotive Series

Emf

Faraday's laws

Galvanometer

Hydrogen electrode

Insulator

Nernst equation

Ohm's law

Oxidation

Oxidizing agent

Potentiometer

Reducing agent

Reduction

Reference electrodes

Resistance

Standard Electrode Potentials, E^o, (volts)

Voltage

Voltaic cells

Weston standard cell

D. PRELIMINARY REPORT - Read through Experiment 6 prior to second laboratory period on electrochemistry. Then complete this PRELIMINARY REPORT.

1. State Faraday's laws in words and in the form of an equation.

2. With the aid of a diagram, describe the potentiometric method for the measurement of electromotive force. (Draw the diagram.)

3. In the formation of chromium metal from Cr^{3+}, the number of grams of Cr produced by the passage of one faraday of electricity equals _____ grams.

4.   Describe the calomel half-cell you are to construct, i.e., draw the half-cell, write the half-reaction, and discuss its construction.

5.   What are the reasons for using the high series resistor in series with the galvanometer when making the initial null adjustments?

6.   What are 2 reasons that activities are used in the equilibrium expression of the Nernst equation rather than concentrations?

7.   What is the relationship between the standard cell cell potential and the equilibrium constant?

YOU SHOULD BE PREPARED TO ANSWER ANY OF THESE QUESTIONS ON A CLOSED BOOK QUIZ.

E.   REFERENCES - See the chapter or experiments on electro-chemistry in your lecture textbook, or other books of your choosing.

1.   Daniels, F., and R. A. Alberty, "Physical Chemistry," John Wiley, New York, 1975, pp. 191-214.

2.   Daniels, et al., "Experimental Physical Chemistry," McGraw-Hill, New York, 1970, pp.178-201.

3.   Metz, C. R., "Theory and Problems of Physical Chemistry," McGraw-Hill, New York, 1976, pp. 130-143.

4.   Sears, F. W., and M. W. Zemansky, "College Physics," Addison-Wesley, Reading, Massachusetts, 1960, pp. 566-568.

5.   Shoemaker, D. P., and C. W. Garland, "Experiments in Physical Chemistry," McGraw-Hill, New York, 1962, p. 444.

F. APPARATUS AND CHEMICALS

The calomel half-cell prepared in Experiment 5, a hydrogen
electrode, potentiometer and associated accessories, and
hydrogen gas tank.

G. INTRODUCTION

Aside from their importance as electrical energy
storage devices and power sources, electrochemical cells
provide a very useful means of determining thermodynamical
functions.

Activity coefficients, free energies and entropies
can be determined by making various electrical measurements
on cells.

The cell in which we will be interested and the one
that yields useful thermodynamical data is a reversible
cell. The term reversible means the same here as in our
study of thermodynamics. Almost all electrochemical cells
involve solutions of some sort. A solution which conducts
an electric current is called an electrolyte, and the non-
spontaneous process is called electrolysis. In electrolysis
electrical energy used to bring about desired chemical
changes involve electrolytic cells. When the chemical
reactions are spontaneous, voltaic cells are involved.

The methods of measuring electrochemical cell
potentials and how standard potentials are defined will
briefly be described. The proper procedure for writing cell
notation will be indicated. A discussion will be presented
on standard (reference) cells. Finally, the relationship of
electrochemical data to thermodynamics will be given.

H. THEORY

FARADAY'S LAWS OF ELECTROLYSIS

According to Faraday's first law, the mass of any
substance deposited or dissolved at an electrode is propor-
tional to the quantity of electricity which passes through
the electrolytic cell. The quantity of electricity can be
expressed as the number of electrons, coulombs, or faradays.
Faraday's second law states that the masses of different
substances deposited or dissolved at an electrode by the
same number of coulombs are proportional to their equivalent
weights.

By definition one coulomb, the unit of electric
charge in the SI system, is equal to one ampere-second and
96,487 coulombs, C, is equal to one faraday, F, which is
equivalent to Avogadro's number of electrons, 6.023×10^{23}.
One faraday is therefore the quantity of electricity which
will reduce one gram-equivalent weight of any substance at

the cathode and oxidize one gram-equivalent at the anode, which amounts to the gain or loss of one mole of electrons.

If the current, I, is maintained for a time, t, in seconds, then the number of faradays of electricity is It/F where F is in coulombs. Therefore, if a mass, w, of a substance of atomic weight, M, with $|z|$ number of charges on the ion is deposited, then we have the following mathematical equation:

$$\frac{w}{M} = \frac{It}{|z|\ F} = \frac{C}{|z|\ F} \qquad \text{(See Example 6-1)} \qquad (6-1)$$

where C equals the number of coulombs.
In summary

1 faraday = 6.023×10^{23} electrons = 96,487 coulombs

1 coulomb = quantity of electricity involved when a current of 1 ampere flows for 1 second. Therfore, Faraday's second law may be expressed as follows: During electrolysis, 96,487 coulombs (1 Faraday) of electricity reduce and oxidize, respectively, one gram-equivalent of the oxidizing agent and the reducing agent.

Imagine three electrolytic cells, all equipped with platinum electrodes, but with different aqueous solutions as electrolytes, as shown in Figure 6-2. To ensure that the current is the same in all cells, they are connected in series. If we maintain a current until 96,487 coulombs have been transferred through each cell, then we find that silver is deposited on the negative electrode of the left-hand cell, copper on the negative electrode of the middle cell, and hydrogen gas is evolved on the negative electrode of the right-hand cell. After calculating the mass of material deposited at each electrode we obtain the following results:
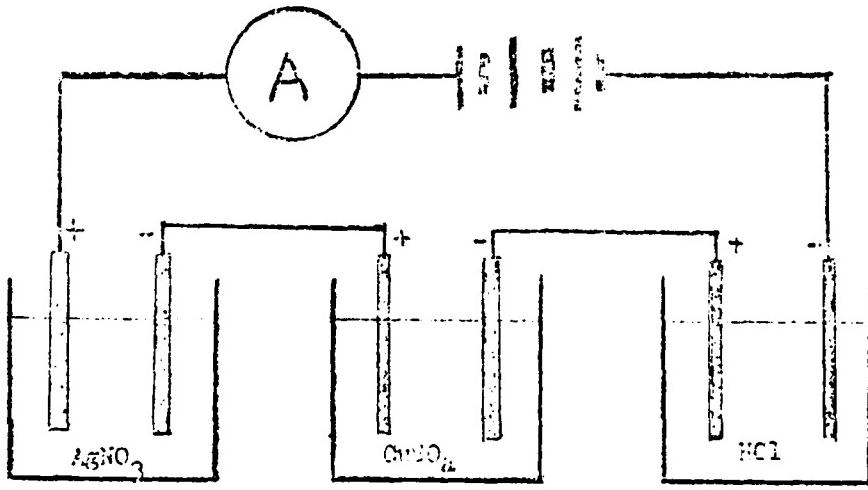

FIGURE 6-2
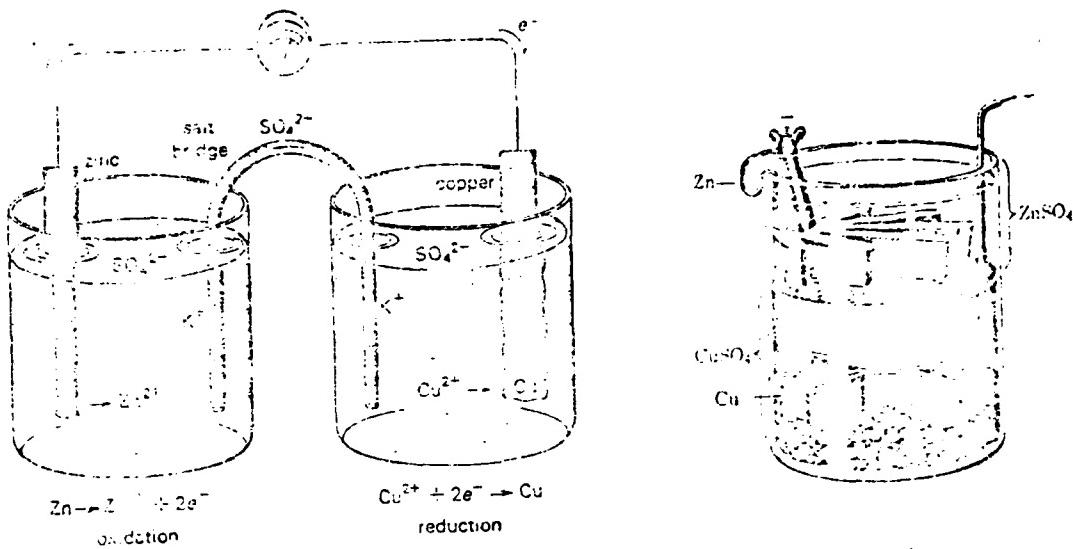
FIGURE 6-3a. Modified Daniell Cell b. Daniell Cell
(Keenan, C.W., J.H. Wood, and D.C. (Sears, 1960, p. 598)
Kleinfelter, "General College Chemistry,"
Harper & Row, New York, 1976, p. 434)

Silver	1 g-atom	= 108 g
Copper	½ g-atom	= 31.8 g
Hydrogen	1 g-atom	= 1.008 g

which agree with Faraday's law calculations (See EXAMPLE 6-1
and PROBLEM 6-1).

ELECTROCHEMICAL CELLS

As we have already said an electrochemical cell is
an arrangement of two electrodes and an electrolyte. Such a
cell capable of producing an electric current as a result of
a chemical reaction within the cell is shown in Figure 6-3b,
the Daniell cell. However, we will review what occurs in a
modified Daniell cell, which consists of a strip of zinc
immersed in a solution of zinc ions and a strip of copper
immersed in a solution of cupric ions, the two solutions
being connected by a U tube (See Figure 6-3a).
This cell consists of two half-cells, a zinc half-
cell and a copper half-cell. When the external circuit is
completed, a current flows and the following reactions take
place:

$$Zn \longrightarrow Zn^{2+} + 2e^-$$
$$Cu^{2+} + 2e^- \longrightarrow Cu.$$
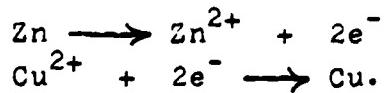
The cell reaction can be divided into two parts, oxidation
(electron loss) and reduction (electron gain). In general,
each electrode involves a junction between a metal and a
solution of the corresponding metal ions.

There exists at the surface between the metal and the solution a difference in potential which is called the electrode potential, or <u>electromotive force, emf</u>, which for a cell is symbolized by $\overline{E}_{cell}$. Where

$$E_{cell} = E_{left} + E_{right} + E_{junction}$$

for which

E_{left} = potential of the left-hand electrode,

E_{right} = potential of the right-hand electrode,

$E_{junction}$ = potential which results from the contact between the solution containing the zinc ions and the solution containing the cupric ions.

For practical purposes, the junction potential may be essentially eliminated by filling the U tube with saturated KCl. Such a device is called a salt bridge. In this case we may write

$$E_{cell} = E_{left} + E_{right}$$

which may be represented by the following electrochemical notation:

$$Zn + Cu^{2+} = Zn^{2+} + Cu$$

$$Zn \mid Zn^{2+} \mid\mid Cu^{2+} \mid Cu$$
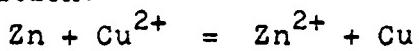
in which the single slash (or bar) implies contact between different phases and the double slash indicates that the junction potential has been rendered neglible by means of a salt bridge.

MEASUREMENT OF ELECTROMOTIVE FORCE

The emf of a cell can't be measured with an ordinary voltmeter because the voltmeter draws an appreciable current from the cell. This changes the concentration of the electrolyte around the electrodes causing an emf change in the cell. Thus, the voltmeter reading will not take into account the internal resistance of the cell.
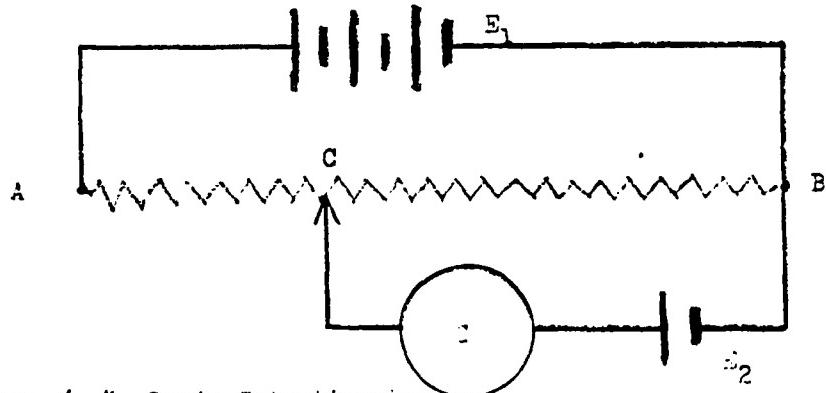
FIGURE 6-4. Basic Potentiometer
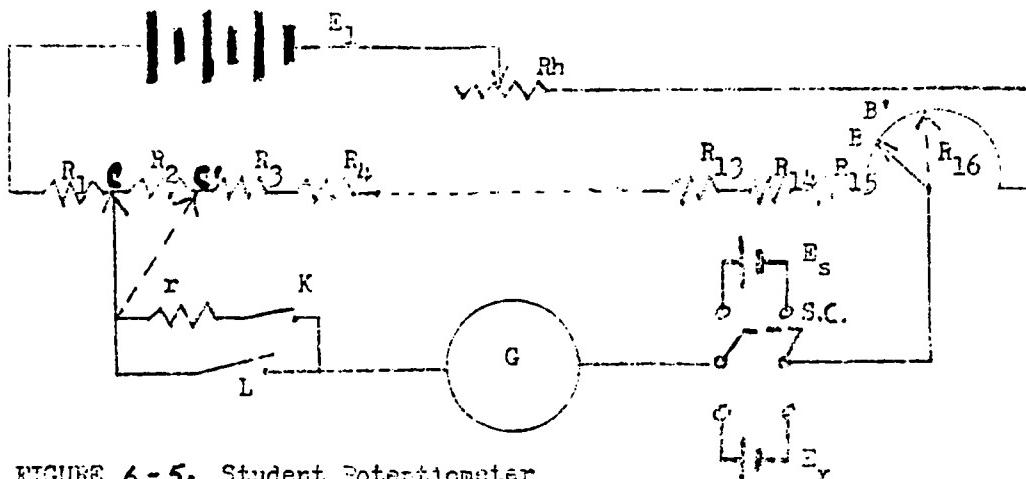
FIGURE 6-5. Student Potentiometer

Therefore, accurate determinations of the emf of a cell must be made under conditions where there is practically no current flow. The potentiometer is an instrument which can be used to measure the emf of a cell without drawing any current from the cell. Essentially, it balances an unknown potential difference against an adjustable, measurable potential difference.

"The principle of a basic potentiometer is shown in Figure 6-4. A resistance wire AB is permanently connected to the terminals of a cell of emf E_1. A sliding contact C is connected through the galvanometer G to a second cell whose emf E_2 is to be measured. Contact C is moved along the wire until a position is found at which the galvanometer shows no deflection." (Sears and Zemansky, 1960, p. 566)

In practice, the simple potentiometer circuit is modified as shown in Figure 6-5 above where a student potentiometer is shown.

The single slide wire of Figure 6-4 is replaced by a 1500 ohm resistor which is tapped every 100 ohms and a 100 ohm slide wire. The movable contacts C and B may include any whole number of resistors plus any fraction of the slide wire. The potentiometer is adjusted so that the upper circuit delivers 0.001 ampere. This corresponds to a potential drop of 0.100 volts per 100 ohms. The emf of the working battery is approximately 3 volts. With this arrangement it is possible to measure to the nearest 0.0001 volt an emf of between 0.0000 and 1.6000 volts.

To ensure that the current in the upper circuit has its proper value the switch is thrown to the E_s position, connecting the standard cell of known emf into the circuit. Contacts C and B are set at the points corresponding to the known voltage of E_s, and then the rheostat R_h is adjusted until the galvanometer G shows no deflection. Then without changing the setting of R_h, the switch is placed in the position connecting the cell of unknown emf, E_x. B and C

are again adjusted until the galvanometer is brought to zero. The unknown emf, E_x, may then be read directly from the positions of C' and B' since

$$\frac{E_x}{E_s} = \frac{\text{Resistance of B' + C'}}{\text{Resistance of B + C}} \qquad (6\text{-}2)$$

NOTE: During preliminary adjustments a protective resistor is inserted in series with the galvanometer to prevent damage both to it and to the standard cell.

STANDARD CELLS

"The electromotive force of the Weston cell in the new absolute system is 1.0186 volts at $20°$. This cell is set up in an airtight H-shaped vessel, with platinum wires sealed through the bottoms for connection with the electrodes, as shown in Figure 6-6. The positive electrode consists of pure mercury, which is covered by a thick paste of mercurous sulfate and a small quantity of cadmium sulfate. The negative electrode is a cadmium amalgam containing 12.5 percent cadmium. On the top of the solidified amalgam and the mercurous sulfate paste are placed some rather large and clear cadmium sulfate crystals; then the cell is filled with a saturated solution of cadmium sulfate. The ends of the tubes are closed, allowing sufficient air space for thermal expansion. The materials must be thoroughly purified. The temperature coefficient of the cell is small, so that the electromotive force may be given with accuracy sufficient for most purposes by the expression; $E_t + E_{20} = 0.0000406(t - 20)$." (Daniels et al. 1970, p. 510)
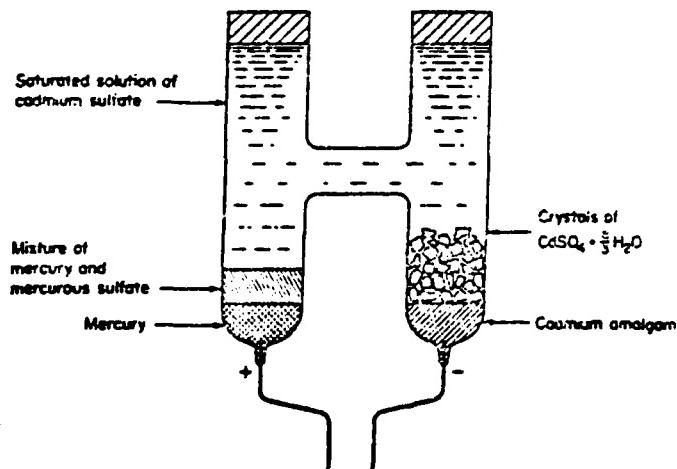

FIGURE 6-6: Weston standard cell
(Moore, W. J., "Physical Chemistry," Prentice-Hall, Englewood Cliffs, New Jersey, 1972, p. 526.)

STANDARD ELECTRODE POTENTIALS, E^o

The term standard electrode potential is used to designate the potential that would be obtained with the constituents present at unit activity. By definition the standard electrode potential of an electrode is given a positive value if this electrode is more positive than the standard hydrogen electrode and a negative sign if it is more negative than the standard hydrogen electrode. The standard hydrogen electrode has arbitrarily been assigned a value of 0.000 volts at 25°C in the same way that heats of formation, $\Delta H^o{}_f$, values are assigned the value of zero for elements in their standard state at 25°C.

Table 6-1 gives standard electrode potentials, E^o, for a number of half-reactions at 25°C. In accordance with IUPAC rules the reactions are written as reductions. This table is sometimes called the electromotive series of the elements and some of its uses are as follows:

1. The elements with relatively large positive electrode potentials are good oxidizing agents when in the oxidized form.

2. The metals with relatively high negative electrode potentials are good reducing agents in the free state.

3. The reduced form of any element will reduce the oxidized form of any element above it in the series.

Thus one can theoretically calculate the emf of a cell by algebraically adding the potential at the anode to the potential at the cathode. All cells are arbitrarily diagramed so that oxidation takes place at the left-hand electrode, the anode. Reduction, therefore, takes place at the right-hand electrode, the cathode. The cell reaction is thus the sum of the two half-cell reactions. If the electrode is used as the cathode, the E^o values are just as they are found in Table 6-1. If the electrodes are used as an anode, then the reaction must be reversed and the sign of the potential in Table 6-1 must be changed. (See EXAMPLE 6-2 and PROBLEM 6-3)

THERMODYNAMICS OF ELECTROCHEMICAL CELLS

In dealing with the energy interrelationships of cells, thermodynamic principles areapplicable if the cells are reversible. A cell is reversible if:

1. No chemical action occurs when the cell is connected to an external potential which exactly balances the potential of the cell, and

TABLE 6-1

STANDARD REDUCTION POTENTIALS (25°C)

Reduction Half-Reaction		E°, Volts
$F_{2(g)} + 2H^+ + 2e^-$	$\rightarrow 2HF$	3.06
$F_{2(g)} + 2e^-$	$\rightarrow 2F^-$	2.87
$O_{3(g)} + 2H^+ + 2e^-$	$\rightarrow H_2O + O_{2(g)}$	2.07
$MnO_4^- + 4H^+ + 3e^-$	$\rightarrow MnO_{2(s)} + 2H_2O$	1.70
$MnO_4^- + 8H^+ + 5e^-$	$\rightarrow Mn^{2+} + 4H_2O$	1.51
$Au^{3+} + 3e^-$	$\rightarrow Au_{(s)}$	1.50
$Cl_{2(g)} + 2e^-$	$\rightarrow 2Cl^-$	1.36
$MnO_{2(s)} + 4H^+ + 2e^-$	$\rightarrow Mn^{2+} + 2H_2O$	1.23
$O_{2(g)} + 4H^+ + 4e^-$	$\rightarrow 2H_2O$	1.23
$Br_{2(\ell)} + 2e^-$	$\rightarrow 2Br^-$	1.07
$2Hg^{2+} + 2e^-$	$\rightarrow Hg_2^{2+}$	0.92
$Ag^+ + e^-$	$\rightarrow Ag_{(s)}$	0.80
$Hg_2^{2+} + 2e^-$	$\rightarrow 2Hg_{(\ell)}$	0.79
$Fe^{3+} + e^-$	$\rightarrow Fe^{2+}$	0.77
$O_{2(g)} + 2H_2O + 4e^-$	$\rightarrow 4OH^-$	0.40
$I_{2(s)} + 2e^-$	$\rightarrow 2I^-$	0.54
$Cu^+ + e^-$	$\rightarrow Cu_{(s)}$	0.52
$Cu^{2+} + 2e^-$	$\rightarrow Cu_{(s)}$	0.34
$Hg_2Cl_2 + 2e^-$	$\rightarrow 2Hg_{(\ell)} + 2Cl^-$ (Saturated)	0.24
$Cu^{2+} + e^-$	$\rightarrow Cu^+$	0.15
$2H^+ + 2e^-$	$\rightarrow H_{2(g)}$	0.00
$Pb^{2+} + 2e^-$	$\rightarrow Pb_{(s)}$	-0.13
$Sn^{2+} + 2e^-$	$\rightarrow Sn_{(s)}$	-0.14
$Ni^{2+} + 2e^-$	$\rightarrow Ni_{(s)}$	-0.25
$Cd^{2+} + 2e^-$	$\rightarrow Cd_{(s)}$	-0.40
$Fe^{2+} + 2e^-$	$\rightarrow Fe_{(s)}$	-0.44
$S_{(s)} + 2e^-$	$\rightarrow S^{2-}$	-0.48
$O_{2(g)} + e^-$	$\rightarrow O_2^-$	-0.56
$Zn^{2+} + 2e^-$	$\rightarrow Zn_{(s)}$	-0.76
$2H_2O + 2e^-$	$\rightarrow H_{2(g)} + 2OH^-$	-0.83
$Mn^{2+} + 2e^-$	$\rightarrow Mn_{(s)}$	-1.18
$Al^{3+} + 3e^-$	$\rightarrow Al_{(s)}$	-1.66
$Mg^{2+} + 2e^-$	$\rightarrow Mg_{(s)}$	-2.37
$Na^+ + e^-$	$\rightarrow Na_{(s)}$	-2.71
$Ca^{2+} + 2e^-$	$\rightarrow Ca_{(s)}$	-2.87
$K^+ + e^-$	$\rightarrow K_{(s)}$	-2.92
$Li^+ + e^-$	$\rightarrow Li_{(s)}$	-3.04

2. <u>The chemical reaction</u>, which takes place when the external potential is lowered an infinitesimal amount, <u>is reversed</u> when the external potential is increased an infinitesimal amount.

Thus we will confine our discussion to reversible cells.

At constant temperature and pressure, the electrical work done by the system per mole of reactant consumed is nFE, in which n is the number of electrons in the reaction, F is the faraday, 96,487 coulombs, and E is the emf of the cell. It should be noted that n and F are independent of temperature. The free energy of the system decrease by an equal but opposite amount, and we may therefore write

$-\Delta G = nFE$, or

$$\Delta G = -nFE. \tag{6-3}$$

This important equation represents the link between thermodynamics and electrochemistry. By means of this equation it is possible to determine thermodynamic quantities from emf measurements.

From the definition of Gibbs free energy

$$dG = -SdT + VdP \tag{6-4}$$

then $\left(\frac{\partial G}{\partial T}\right)_P = -S$, or for changes associated with some

process,

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S. \tag{6-5}$$

Using Equation 6-3 we can write

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -nF(\partial E/\partial T)_P$$

or $\Delta S = nF(\partial E/\partial T)_P$ (6-6)

Knowing ΔG and ΔS, we can calculate ΔH from the Gibbs-Helmholtz equation:

$$\Delta G = \Delta H + T(\partial \Delta G/\partial T)_P \tag{6-7}$$

or

$$\Delta H = -nFE + nFT(\partial E/\partial T)_P \tag{6-8}$$

Equation 6-8 relates the heat of the reaction occurring within the cell as a function of the emf and the temperature coefficient of the emf. Since emf measurements are usually more precise than thermal measurements, heats of reaction determined by Equation 6-8 are often more accurate than the same quantities determined from calorimetric measurements (See EXAMPLE 6-3 and PROBLEM 6-4).

Since $\Delta G = -nFE$, it is clear that if E is positive then ΔG will be negative and the corresponding chemical reaction will be spontaneous. Therefore, the sign of E

tells us whether a cell is spontaneous in the direction it is written.

The last major topic of electrochemistry is the calculation of chemical equilibria from emf measurements. This topic together with a discussion of activity is now presented. It should be reviewed again when performing Experiment 7.

ELECTROMOTIVE FORCE AND CHEMICAL EQUILIBRIA

This section will attempt to show that the emf of a cell depends on the concentration, or more precisely on the activity, of the reagents in a reaction. Consider an electrochemical cell for which the overall chemical reaction is

$$cC + dD = gG + hH. \tag{6-9}$$

For 1 mole of reagent C the free energy can be expressed as

$$G_C = G_C^o + RT \ln(a_C)$$

where a_C equals the activity of C. For c moles of reagent C we have

$$cG_C = cG_C^o + cRT \ln(a_C)$$

$$= cG_C^o + RT \ln(a_C)^c$$

For the reaction represented by Equation 6-9 involving c moles of C, d moles of D, g moles of G, and h moles of H the change in Gibbs free energy is given by

$$\Delta G = \Delta G^o + RT \ln\frac{(a_G)^g(a_H)^h}{(a_C)^c(a_D)^d} \tag{6-10}$$

where the a's represent the activities of the reactants and products under a given set of conditions, and ΔG^o is the difference in free energy of the products and the reactants when all reagents are in their standard states.

Substituting Equation 6-3 for ΔG, and ΔG^o, i.e.,

$$\Delta G = -nFE \text{ and}$$

$$\Delta G^o = -nFE^o \text{ into Equation 6-10 we get,}$$

$$-nFE = -nFE^o + RT \ln Q$$

where Q = the activity quotient or

$$E = E^o - \frac{RT}{nF} \ln Q. \tag{6-11}$$

Equation 6-11 is commonly referred to as the Nernst equation.

At $25^{\circ}C$

$$E = E^{\circ} - \frac{(8.314)(298.1)(2.303)}{n(96,487)} \log Q$$

$$= E^{\circ} - \frac{0.0591}{n} \log Q$$

The Nernst equation gives the electromotive force of a cell as a function of the initial and final activities. However, when the activity of all the reagents are unity, the logarithmic term drops out and $E = E^{\circ}$.

If the reaction takes place under equilibrium conditions $\Delta G = 0$ and thus $E = 0$ giving

$$E^{\circ} = \frac{RT}{nF} \ln K \qquad\qquad (6\text{-}12)$$

where K is the equilibrium constant for the reaction in Equation 6-9.

This section deals with one of the most important areas in electrochemical calculations. You will use these concepts in experiments 6 and 7. Therefore, it is important you have a good understanding of these concepts. The PROBLEMS AND EXAMPLES at the end of Experiment 7 will help in the development of this understanding.

The discussion of activities is a complex topic in itself and will only be considered briefly. For a more in depth treatment see the applicable sections in your lecture textbook.

ACTIVITIES OF ELECTROLYTES

Activities may be viewed as effective concentrations. They are frequently related to molal concentrations. When this is the case the components in a solution are related by the following equation:

$$a = m\gamma$$

where

    a = activity
    m = molality
    γ = activity coefficient

For dilute solutions of nonelectrolytes there is little difference between activities and concentrations. However, for concentrated solutions of electrolytes the interionic forces of attraction cause large deviations from ideal behavior. For dilute solutions there are no appreciable deviations for either activities or concentrations.

For any electrolyte $M^{v+}X^{v-}$, where v is the magnitude of the charge on the ion, it is not possible to determine single-ion activity coefficients by normal thermodynamic methods, therefore, it is necessary to use the mean ionic

activity coefficients which <u>can</u> be calculated experimentally. These values may be looked up in a reference source. In general, the mean ionic activity is given by

$$a_{(M^{v+}X^{v-})} = (v_+ m\gamma_+)^{v+}(v_- m\gamma_-)^{v-}.$$ (6-13)

Consult your lecture textbook for additional information.
For the problems assigned in this unit you will be given the activities or you may assume that the solutions are dilute and that concentrations may be substituted for activities.

I. PROCEDURE

Preparing the instrument for use

1. Study the schematic diagram in Figure 6-7, then assemble and connect the various parts of the potentiometric apparatus to the potentiometer as described below. CAUTION: Do not tip or shake the Weston cell. It can be ruined easily if not handled with care.

2. Place the double pole double throw switch to E_s. Set the potentiometer at the voltage of the standard cell corrected to room temperature, about 1.01864 volts. If another value is stated by manufacturer, set potentiometer accordingly.

3. Close the circuit by tapping key K lightly; adjust Rh until a minimum deflection of galvanometer, G, is observed. (K is fitted with a high series resistance, r, to assure that only small currents flow in the potentiometer circuit. If high current were drawn from the Weston cell it would be temporarily polarized; if high current were permitted to reach G, its coils might be burned out.)

4. Refine the adjustment just made while tapping key L. (L should be used for fine adjustment only, since it is not fitted with a series resistance.) The potentiometer is now calibrated directly in volts.

Procedure for measurement of an unknown emf

5. Connect the source of unknown emf to the proper terminals. Place the switch to E_x. Be sure that Rh is left at the setting obtained in step 4.

6. Close the circuit by tapping key K; adjust the potentiometer dials until no deflection is observed in G.

7. Refine the adjustment just made while tapping key I The potentiometer reading is the emf of X.
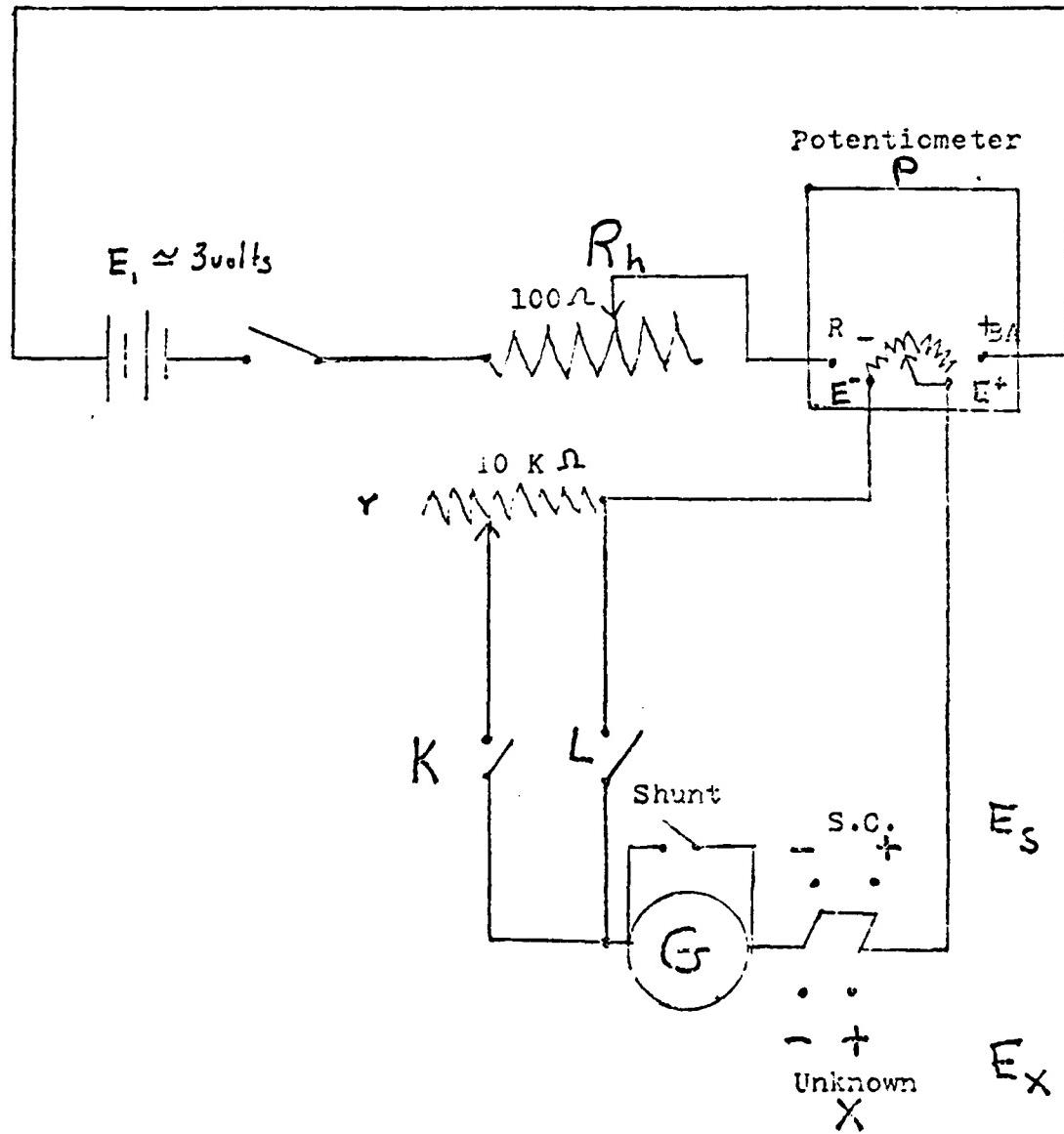
FIGURE 6-7   Schematic for Potentiometer Use

8. Determine the emf of a Daniell cell, and/or those of several other cells to be provided by the instructor. Include the values obtained in your report.

NOTE: Certain difficulties may be encountered in using a potentiometer. If it is impossible to obtain a balance with the unknown cell, reverse the connections as the polarity may be opposite to that assumed. It is also possible but not probable that the emf of the cell is larger than 1.6 volts. Finally, if it is impossible to obtain a galvanometer deflection at any setting of the potentiometer, then look for a loose connection or a broken wire.

The working cell should be checked against the standard cell about every half hour in order to correct for any change in its voltage. Read the directions for the operation of the potentiometer. Make all connections but do not insert the batteries or cells until the instructor has approved the hookup.

Procedure for calibrating your calomel electrode.

The variables that must be experimentally determined in order to calculate the calomel electrode potential are as follows: cell potential, solution temperature, atmospheric pressure and polarity of the electrodes. Using the Nernst equation the potential of the hydrogen electrode is calculated and then the potential of the calomel electrode is found by difference.

Calomel Electrode
(See Figure 5-1)
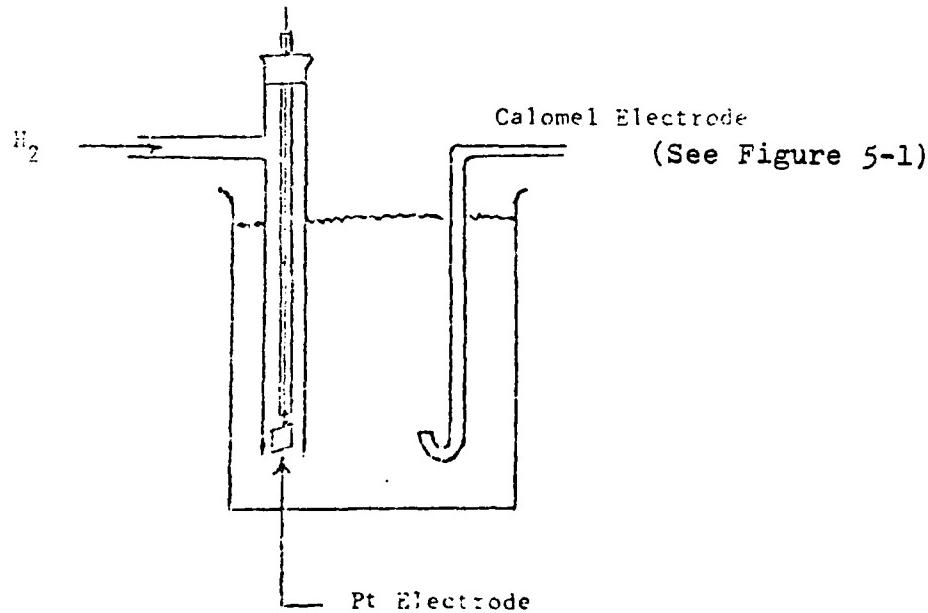
Pt Electrode

FIGURE 6-8: Cell (See also Figure 5-1)

9. Assemble a hydrogen-calomel electrode cell as shown in Figure 6-8. Do not handle the platinum electrodes provided or they may be "poisoned." If necessary use the separate procedure provided on this page for electroplating the platinum electrode with platinum black.

10. Repeat steps 5-7 using your hydrogen-calomel cell. The hydrogen electrode is supplied with electrolytic tank gas and the rate of flow adjusted so that 2-3 bubbles of gas per second are obtained.

NOTE: The calomel electrode should be connected to the positive side of the potentiometer.

PREPARING PLATINUM ELECTRODES

"For depositing platinum black a solution of 3 g platinic chloride and 0.2 g lead acetate in 100 mL of distilled water is prepared. This can be kept in a glass-stoppered bottle and used repeatedly. The platinum electrode should be treated with warm aqua regia (one part concentrated HNO_3 to three parts concentrated HCl) to clean the surface and, if necessary, to remove old platinum black. It is then rinsed thoroughly with distilled water. While still wet the electrode is immersed in (or the cell filled with) the platinizing solution. If there is only one electrode to be treated, platinum wire will serve as the anode. Two dry cells and a rheostat in series are connected between the electrodes, the electrode to be platinized being the cathode (negative). The rheostat is adjusted so that gas is produced only slowly. If both electrodes are to be platinized, the polarity is reversed every 30 seconds. The electrolysis should be stopped as soon as the electrodes are sooty black; an excessive deposit should be avoided. The platinic chloride solution is then returned to its stock bottle; the electrodes are rinsed thoroughly in distilled water, and electrolysis is continued with a very dilute solution of sulfuric acid in order to remove traces of chlorine. After a final washing with distilled water the electrodes are ready for use. After use they should be stored in contact with water; they should never be allowed to dry out." (Shoemaker and Garland, 1962, p. 444)

J.   SPECIAL INSTRUCTION FOR A COMBINED REPORT ON EXPERIMENTS
5 and 6

1.   DRAWING: Illustrate the cells employed. Indicate
polarity, direction of electron flow, cathode, anode, etc.

2.   THEORY: Since your exposure to electrochemistry will be
limited to the laboratory portion of the course, the theory
should be expanded and more comprehensive than any of your
past experiments. Your discussion should include such
things as the theoretical aspects of the electrodes and
cells constructed, and the effects of temperature and
pressure on cell operation. Since you will have other
experiments that necessitate the use of the potentiometer,
you are expected to know the whats, hows, and whys of a
potentiometer. A discussion on the operation of a
potentiometer should therefore be included in your theory
section.

3.   CALCULATIONS: Show all calculations concerned with the
determination of your calomel electrode potential.

4.   Discuss the various factors that may cause the electrode
potential obtained in your experiment to be different from
those predicted theoretically.

K.   CALCULATIONS

1.   Measure the emf of your cell several times and report
the average.

2.   Prepare a Daniell cell and/or other cells (dry cells)
provided by the instructor and measure the emf of them
several times and report the average for each cell.

3.   Check the pH of the solution and determine the
hydrogen ion concentration from the pH.

4.   Write the half-cell equations and then the overall cell
equation for your hydrogen-calomel cell.

5.   Calculate the theoretical standard emf for your cell
assuming uni   ctivity.

6.   From the measured emf of your cell and the calculated
emf of the hydrogen electrode, calculate the potential of
the calomel electrode by difference.

7.   From your data and the Nernst equation calculate the
potential of the hydrogen electrode.

L. EXAMPLES AND PROBLEMS

EXAMPLE 6-1: (Metz, 1976, p. 140) What is the minimum mass of reactants for a dry cell if it is to generate 0.0100 A for 10.0 hr?

Using Equation 6-1, $\dfrac{w}{M} = \dfrac{It}{|z|F} = \dfrac{C}{|z|F}$

$C = It = (0.0100 \text{ A})(10.0 \text{ hr})(3600 \text{ sec/hr}) = 360 \text{ C}$

$|z|$ is obtained from the half reactions

$Zn = Zn^{2+} = 2e^-$ $|z|$ for Zn = 2

$2MnO_2 + NH_4^+ + 2e^- = Mn_2C_3 + NH_3 + OH^-$ $|z|$ for MnC_2 = 1
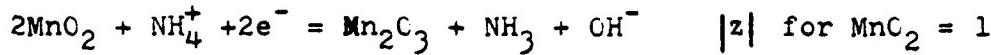
$w(Zn) = \dfrac{CM}{|z|F} = \dfrac{(360 \text{ C})(65.37 \text{ g/mole})}{2(96,487 \text{ C/mole})} = \underline{0.122 \text{ g Zn}}$

$w(MnC_2) = \dfrac{(360 \text{ C})(86.94 \text{ g/mole})}{1(96,487 \text{ C/mole})} = \underline{0.324 \text{ g } MnC_2}$

where w = weight

EXAMPLE 6-2: Give the cell reaction and calculate the emf for the following cell at $25^{\circ}C$.

$$Ag \,\Big|\, Ag^+_{(a=1)} \,\Big|\Big|\, Cu^{2+}_{(a=1)} \,\Big|\, Cu$$
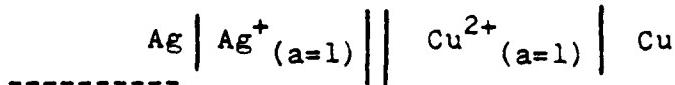
The half-cell reactions are:

$2Ag = 2Ag^+ + 2e^-$
$Cu^{2+} + 2e^- = Cu$
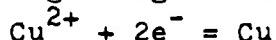
giving the following cell reaction

$2Ag + Cu^{2+} = 2Ag^+ + Cu$

$E^O = E^O_{left} + E^O_{right}$
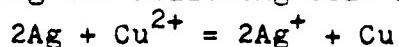
$E^O = (-0.80) + (+0.34) = \underline{-0.46 \text{ volts.}}$

NOTE: Since the silver half-cell occurs as an oxidation, the sign of the value in Table 6-1 must be changed. The cell is not spontaneous as written.

EXAMPLE 6-3: Given the following cell and associated data:

$$Ag \,\Big|\, AgAc_{(s)} \,\Big|\Big|\, Cu(Ac)_{2 \, (0.1m)} \,\Big|\, Cu$$
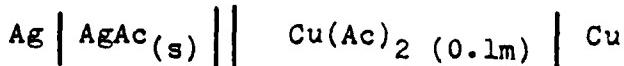
where Ac denotes acetate ion and

$E_{298} = -0.372$ volt

$E_{308} = -0.374$ volt.

Calculate ΔG, ΔS, and ΔH at $25^\circ C$ for the reaction

$$2Ag + Cu^{2+}_{(0.1m)} + 2Ac^-_{(0.2m)} = 2AgAc_{(s)} + Cu.$$
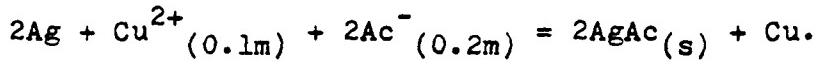
$\Delta G = -nFE^o = -2(96,487)(-0.372) = \underline{7.18 \times 10^4 \text{ joules}}$

E changes by -0.002 volt in $10^\circ C$, since the potential does not change that drastically we can approximate as follows:

$(dE/dT) = -0.0002$

and since $\Delta S = nF(dE/dT) = 2(96,487)(-0.0002)$

$$= \underline{-38.5 \text{ joules/degree}} \qquad \text{(only 1 SF)}$$

and since $\Delta H = \Delta G + T\Delta S$

$$= 7.18 \times 10^4 + + 298(-38.5) = 6 \times 10^4 \text{ joules} \qquad \text{(1 SF)}$$

NOTE: The answers do not reflect the correct number of SF. The problem is concerned with the value of 0.0002.

PROBLEM 6-1: A current of 0.100 ampere flows for 100 seconds through a solution of $Pb(NO_3)_2$ in a cell. How many grams of lead are deposited at the cathode?

PROBLEM 6-2: Balance the following oxidation-reduction reaction:

$$Al_{(s)} + H_2O_{(1)} \xrightarrow{(OH^-)} Al(OH)_6^{3-}{}_{(aq)} + H_2{}_{(g)}$$
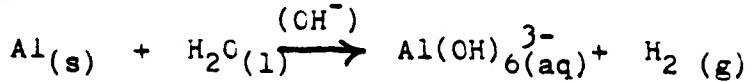
PROBLEM 6-3: Draw and label the electrochemical cell which corresponds to the following reaction at $25^{\circ}C$.

$$Zn + Br_2 = Zn^{2+}_{(a=1)} + 2Br^-_{(a=1)}$$
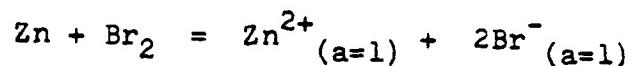
Calculate the potential of the cell. Is this a spontaneous reaction?

PROBLEM 6-4: Calculate ΔG°, ΔS°, and ΔH° for the following cell:

$$Pt, H_2 \mid H^+ \mid\mid AgCl \mid Ag$$
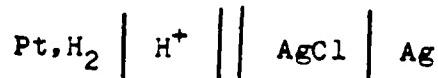
which has a standard emf of 0.2224 volt at $25^{\circ}C$ (assume unit activities) and a temperature coefficient of $-0.000645 \frac{volt}{^{\circ}C}$. The cell reaction is

$$AgCl + \tfrac{1}{2}H_2 = Ag + H^+_{(a=1)} + Cl^-_{(a=1)}$$
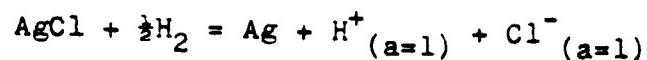
EXPERIMENT 7: POTENTIOMETRIC TITRATIONS WITH HYDROGEN

A. STUDY GUIDE AND REVIEW ASSIGNMENT

1. Reread the section entitled ELECTROMOTIVE FORCE AND
CHEMICAL EQUILIBRIA in Experiment 6.

2. Read the THEORY AND PROCEDURE sections of Experiment 7.

3. Complete the PRELIMINARY REPORT for this experiment
prior to coming to lab.

4. Supply definitions for the KEY WORDS. The majority
of these terms should be discussed in your lecture textbook.

5. Work the following problem which was taken from Daniels
and Alberty (1975, p. 216):

     When a hydrogen electrode and normal calomel
electrode are immersed in a solution at $25^{\circ}C$ a potential
of 0.664 volts is obtained. Calculate (a) the pH and
(b) the hydrogen-ion activity.

ANS: (a) 6.50, (b) 3.16×10^{-7}

B. OBJECTIVES - You shall be able to:

1. Define and/or briefly discuss the KEY WORDS.

2. Use the Nernst equation to calculate cell volatges, ion
concentrations or activities for cells operating at other
than standard conditions, e.g., see PROBLEM 7-3.

3. Write an equation to show the relationship between a
standard cell voltage and the equilibrium constant of the
cell reaction, and use it to solve related problems such as
PROBLEM 7-2 at the end of this experiment.

C. KEY WORDS: Supply operational definitions for

Acid-base titration

Activity quotient, Q

Equivalence point

Equivalents

pH

Potentiometric titration

Titration

D. PRELIMINARY REPORT - Read through Experiment 7 prior to
the third laboratory period on electrochemistry. Then
complete this PRELIMINARY REPORT.

1. What is the main reason why activities are used in the
equilibrium expression of the Nernst equation rather than
concentrations?

2. Write the electrochemical notation for the cell you are
to construct in Experiment 7. Explain this diagram in
writing.

3. Why should you avoid placing the platinized electrode
in contact with strongly basic solutions?

4. Give a brief definition of the word potentiometer.
Give a short explanation of the operation of a potentiometer
as used in these experiments.

E. REFERENCES - See the chapter on electrochemistry in your
lecture textbook or other books of your choosing.

1. Daniels, F., and R. A. Alberty, "Physical Chemistry,"
John Wiley, New York, 1975, pp. 191-211.

2. Daniels, et al., "Experimental Physical Chemistry,"
McGraw-Hill, New York, 1956, pp. 168-199.

3. Metz, C. R., "Theory and Problems of Physical Chemistry,"
McGraw-Hill, New York, 1976, pp. 130-147.

4. Wilson, et al., "Experiments in Physical Chemistry,"
Pergamon Press, New York, 1968, pp. 116-118.

F. APPARATUS AND CHEMICALS

Potentiometer and accessories; hydrogen electrode; the
calomel electrode prepared in Experiment 5; 0.50 $\underline{N}$
standardized HCl solution; 0.05 $\underline{N}$ sodium hydroxide solution;
burette, 250 mL beaker, magnetic stirrer and stirring bar;
hydrogen gas; and acetic acid solution unknown.

G. PURPOSE

1. To use the 0.1 N calomel electrode (decinormal) you prepared as a reference electrode, and

2. To use the electrochemical techniques to follow the course of an acid-base titration.

H. THEORY

The general theory for this experiment is included in Experiment 6 of this UNIT. These pages should be reviewed before continuing with Experiment 7. However, the theory is summarized here.

As previously mentioned in Experiment 6 of this Unit; at constant temperature and pressure, the free energy change which accompanies the occurrence of a chemical reaction in a galvanic cell is related to the cell potential by the relation

$$\Delta G = -nFE. \tag{7-1}$$

This is the same as equation 6-3. E is the emf of the cell, n is the number of equivalents of chemical change, and F is a conversion factor between the electrical units commonly employed for nE and the thermal units in which F is usually expressed; F is also known as the Faraday.

At constant temperature and pressure the free energy change is related to the standard free energy change by the equation

$$\Delta G = \Delta G^{o} + RT \ln Q \tag{7-2}$$

where Q, the activity quotient, is the product of the activities of the products in their final states divided by the product of the activities of the reagents in their initial states, each activity being raised to the power of the appropriate stoichiometric coefficient associated with a balanced equation.

$$E = E^{o} - \frac{RT}{nF} \ln Q \tag{7-3}$$

In this experiment the cell which will be employed is represented by

$$Pt \left| H_2, H^+_{(\underline{m}=x)} \right| \left| KCl_{(\underline{m}=0.100)}, Hg_2Cl_2 \right| Hg$$
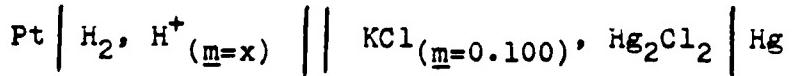
The left hand member of this cell is the hydrogen electrode; the symbol x indicates the molality of hydrogen ion. The double bar indicates that a salt bridge is employed to connect the two half-cells; it will be assumed

that the use of the salt bridge eliminates liquid junction potentials. The right-hand member of the cell is the decinormal calomel electrode.

The emf of this cell can be expressed in the form of Equation 7-3 as

$$E = E^O - \frac{RT}{F}\ln\frac{[H^+][Cl^-]}{(P_{H_2})^{\frac{1}{2}}} \qquad (7-4)$$

where P_{H_2} is the pressure of hydrogen, and the quantities in the numerator of the expression for Q are understood to represent activities rather than concentrations.

The net reaction in the cell,

$$\tfrac{1}{2}H_{2(g)} + \tfrac{1}{2}Hg_2Cl_{2(s)} = H^+_{(aq)} + Cl^-_{(aq)} + Hg_{(l)}$$
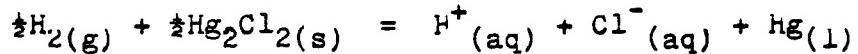
is the sum of the processes occurring at the two electrodes. Similarly, the E^O for the cell is the sum of the E^O values for the half-cell reactions. These are:

$$\tfrac{1}{2}H_2 = H^+ + e^- \qquad E^O = 0.0000 \text{ volt,}$$

when the pressure of H_2 is one atmosphere ($a_{H_2} = 1$) and the

activity of hydrogen ions is unity, and

$$\tfrac{1}{2}Hg_2Cl_2 + e^- = Hg + Cl^- \qquad E^O = 0.2676 \text{ volt.}$$

For the whole cell, then, $E^O = 0.2676$ volt at 25^OC.

The hydrogen electrode will be operated at essentially 1 atm. pressure. The concentration of chloride ion in contact with the calomel is known, and so is the activity coefficient of this ion, given as 0.772. This allows us to rewrite Equation 7-4 in the form

$$E = E^O - (RT/F)\ln[H^+] - (RT/F)\ln[Cl^-]. \qquad (7-5)$$

At 25^OC the factor $(RT/F)\ln[Cl^-]$ can be replaced by $0.5915 \log[Cl^-]$; where $[Cl^-] = m = 0.100(0.772)$. These substitutions convert Equation 7-5 into

$$E = E^O - 0.05915 \log[H^+] + 0.0656.$$

Substituting 0.2676, for E^O, gives the following:

$$E = 0.3332 + 0.05915(-\log[H^+]). \qquad (7-6)$$

The term $-\log[H^+]$ in Equation 7-6 is called pH. Solving for pH gives

$$pH = \frac{E - 0.3332}{0.05915}. \qquad (7-7)$$

The definition of pH just given involves assumptions as to the magnitudes of certain quantities. The liquid junction potential is neglected, and a best approximation to the value of the single-ion activity coefficient is used in the case of chloride ion. These approximations are required in order to retain the conceptual definition $pH = -\log [H^+]$. Present usage is such that an operational definition of pH is to be preferred; i.e., it should be defined in terms of quantities which are directly measurable. In this case pH is defined in terms of an equation whose form is that of Equation 7-7; the constant terms in this relation involve only experimental values of the standard electrode potentials, liquid junction potentials, mean activity coefficients, etc. Portable, rugged instruments, i.e., pH meters, are now available which make use of the above theory and are calibrated to read pH directly.

During the titration that you are about to perform, a sharp change in potential of ph is obtained at the end-point. A typical plot of E (or pH) versus mL of base added is shown in Figure 7-1. The equivalence point corresponds to the inflection point on the graph.
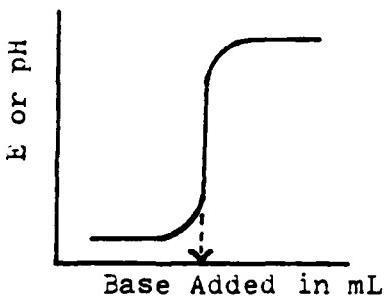
FIGURE 7-1

A more sensitive means of detecting the equivalence point is to plot $\Delta E/\Delta mL$ (or $\Delta pH/\Delta mL$) versus mL of base added as shown in Figure 7-2. The equivalence point co corresponds to the peak of the curve.
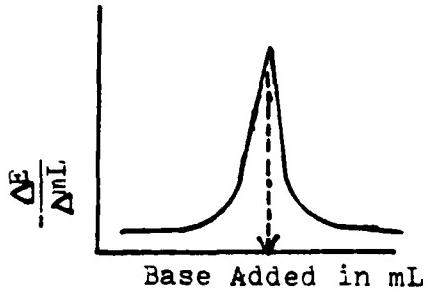

FIGURE 7-2

I. EXPERIMENTAL PROCEDURE

1. Half fill a 250 mL beaker with distilled water. Place the hydrogen electrode, the stirrer bar, and the dipping arm of the calomel half cell in the water.

2. Rinse and fill the burette with NaOH solution of unknown concentration. Place the burette in a location so that portions of the alkali solution may be easily added to the beaker.

3. Start the stirrer. Start the flow of hydrogen gas through the hydrogen electrode; the rate should be adjusted so that no splashing of the solution occurs. A flow rate of 2-3 bubbles per second will be found satisfactory. NOTE: The hydrogen electrode should be tilted slightly so that, as the gas bubbles through, the level of the liquid is never completely above or below the platinized surface. It is VERY IMPORTANT that the platinized electrode surface be kept wet at all times and that you DO NOT touch the electrode surface.

4. Pipette exactly 25 mL of standardized HCl solution into the water in the beaker. Record the final concentration of the HCl solution. (It may be necessary to raise the hydrogen electrode.) Connect the electrodes to the potentiometer.

5. When five minutes have elapsed since the addition of acid, determine and record the emf of the cell.

6. Add 5 mL of NaOH solution to the beaker. When the cell reaches equilibrium, determine and record its emf.

7. Add successive portions of NaOh solution to the beaker; after each addition determine and record the equilibrium emf of the cell. The quantity of alkali solution to be added at any time depends upon the rate of change of the emf. Near the end point of the acid-base reaction, the change in emf for the addition of ONE DROP of NaOH solution will be quite large. It is of considerable help, in this regard, to make a rough plot of emf versus burette reading while the measurements are being made, or a preliminary titration may be performed in order to determine the region where the pH changes most rapidly.

8. DO NOT add more than 2 mL of base in excess of that equivalent to the acid present. Strongly basic solutions cause deterioration of the platinized surface.

9. Repeat steps 4 through 8, but with acetic acid of unknown concentration instead of the standardized HCl solution.

J. CALCULATIONS

1. Use Equation 7-6 to calculate the emf of the cell
employed for several values of pH between 1 and 10.

2. Then plot emf as abscissa versus pH as ordinate. Use
the curve which results to convert each emf observed to the
corresponding pH.

3. For each titration make a plot of pH as ordinate versus
mL of base added as abscissa. The equivalence point of the
titration is at the point of inflection of this plot.
Indicate the equivalence point on each graph.

4. Plot ΔpH/ΔmL versus mL of base added. Find the
equivalence point and compare with step 3.

5. From the number of mL of base added at this point,
compute the normality of the NaOH solution, or the acetic
acid solution, as the case may be.

6. For each titration determine and record the pH at the
equivalence point.

7. Perform a maximum error analysis treatment as outlined
in the UNIT on treatment of errors.

8. Work the PROBLEMS found at the end of this experiment
and include them with your report.

K. SPECIAL INSTRUCTIONS FOR DOING YOUR LABORATORY REPORT

1. As in Experiment 6 you should include a drawing of
your apparatus.

2. The theory should be primarily concerned with the
Nernst equation and how it can be arranged to solve for pH.

3. The graphs should be placed at the end of your report.
They should be labeled in accordance with the directions
in the treatment of errors UNIT.

L. EXAMPLES AND PROBLEMS - Use Table 6-1 as needed.

EXAMPLE 7-1: Calculate the equilibrium constant for the following reaction at 25°C.

$$Ni_{(s)} + Sn^{++}_{(aq)}(a=1) = Sn_{(s)} + Ni^{++}_{(aq)} \ (a=1)$$

$$Ni = Ni^{++} + 2e^- \qquad\qquad E^o = 0.250 \text{ volts}$$
$$Sn^{++} + 2e^- = Sn \qquad\qquad E^o = -0.140 \text{ volts}$$

$$Ni \ \Big| \ Ni^{++}_{(a=1)} \ \Big|\Big| \ Sn^{++}_{(a=1)} \ Sn \qquad \text{which can also be}$$
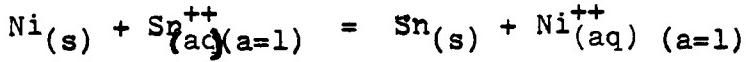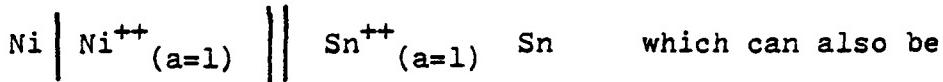
written as follows:

$$Ni;Ni^{++}(a=1) \ \Big|\Big| \ Sn^{++}(a=1);Sn.$$

$$E^o_{cell} = (+0.250) + (-1.140) = +0.110 \text{ volt.}$$

$$E^o = \frac{RT}{nF}\ln K, \quad \text{or} \qquad\qquad E^o = \frac{0.0591}{n}\log K.$$

$$0.110 = \frac{0.0591}{2}\log K.$$

$$\log K = 3.72.$$

$$K = 5250.$$

EXAMPLE 7-2: (Metz, 1976, p. 138) What is E for the cell $Ag/AgBr(s),Br^-(a=0.34) \ // \ Fe^{3+}(a=0.1),Fe2^+(a=0.02)/Pt$ if the standard half-cell reduction potentials are .0713 V for $AgBr/Ag$ and 0.770 V for Fe^{3+}/Fe^{2+}?

Writing the equations and half-cell voltages gives

$$Ag(s) + Br^-(a=0.34) = AgBr(s) + 1e^- \qquad E^o = -0.0713 \text{ V}$$
$$Fe^{3+}(a=0.1) + 1e^- = Fe^{2+}(a=0.02) \qquad E^o = 0.770 \ \text{ V}$$

and adding gives

$$Ag(s) + Fe^{3+}(a=0.1) + Br^-(a=0.34) = AgBr(s) + Fe^{2+}(a=.02)$$
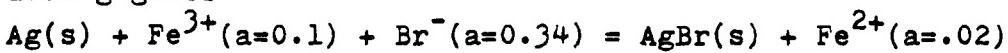
$$E^o = \underline{0.669 \text{ volts}}$$

Observe that the half-cell with the larger reduction potential was written as the reduction reaction, making the overall voltage positive (spontaneous reaction) at standard conditions.

$$Q = (a_{AgBr})(a_{Fe}2+)/((a_{Ag})(a_{Fe}3+)(a_{Br}-))$$

$$= (1)(0.02)/((1)(0.1)(0.34)) \qquad = \underline{0.588}$$

and using Equation 6-11 gives

$$E = 0.699 - \frac{0.059157}{1}\log(0.588) = 0.699 + 0.014 = \underline{0.713 \text{ volts}}$$

The positive value for E implies the reaction is spontaneous as written and the larger value indicates that it is even more so than at standard conditions.

EXAMPLE 7-3: As a review problem, calculate the pH for the following solutions with the concentrations as given:

    a. 0.010 $\underline{M}$ HCl

    b. 2.0 $\underline{M}$ HCl

The pH value is the negative power to which 10 must be raised to equal the hydrogen ion concentration.

$$[H^+] = 10^{-pH}$$
$$pH = -\log[H^+]$$

a. $pH = -\log[H^+] = -\log 10^{-2} = -(-2) = 2$

b. $pH = -\log 2.0 = -.301$

This example serves to remind you that for very concentrated solutions it is possible to have negative pH values.

PROBLEMS 7-1: Derive:

$$E = E^o - \frac{RT}{nF}\ln Q \qquad \text{(Equations 7-1 and 7-2)}$$

PROBLEM 7-2: Calculate K for the following reaction at 25^oC.

$$Ag + Fe^{3+}(a=1) = Ag^+(a=1) + Fe^{2+}(a=1)$$

What would be the potential of the cell if the activity of Ag^+ were 0.1 instead of 1?

PROBLEM 7-3: (Metz, 1976, p. 143) What is E for the cell at $25^{\circ}C$,

$$\text{Mg} \mid \text{Mg}^{2+}(a=10^{-3}) \mid\mid \text{H}^{+}(a=10), \text{H}_2(0.1 \text{ atm}) \mid \text{Pt}$$

if the standard half-cell reduction potentials are -2.375 V for $\text{Mg}^{2+} \mid \text{Mg}$ and 0.000 V for $\text{H}^{+} \mid \text{H}_2$?
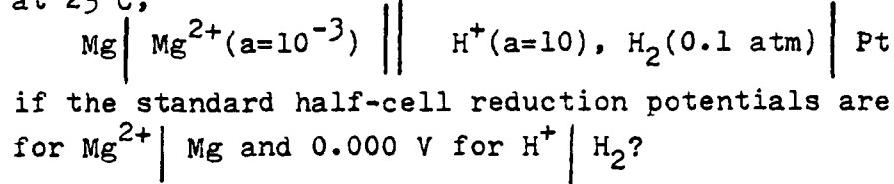
PROBLEM 7-4: For a certain solution $a_{\text{H}^+} = 3 \times 10^{-4}$. Calculate the pH.

PROBLEM 7-5: A very common electrochemical phenomenon is that of corrosion, where substances in contact with a solution form a voltaic cell. Electrochemical calculations can be made to predict whether or not corrosion will occur such as in the following problem:

Would it be safe to store chlorine Cl_2, in an aluminum container? Why or why not? Show your reasoning!

APPENDIX   G

ADSORPTION OF ACETIC ACID BY CHARCOAL

EXPERIMENT 8: ADSORPTION OF ACETIC ACID BY CHARCOAL

A. STUDY GUIDE - Complete the following <u>prior to</u> lab.

1. Read Surface Thermodynamics (Interfaces) chapter to obtain an overview of Adsorption as contained in your lecture textbook.

2. Work the following problems to obtain an understanding of surface phenomenon:

    a. What is the surface area of a cube 1 cm on a side?

    b. If a cube 1 cm on a side is reduced to cubes each 0.1 cm on a side, what is the total surface area of the cubes?

    c. If the cubes are reduced further until each edge is 10^{-7} cm what is then the total area of all the surfaces?

<u>ANS</u>: a. 6 cm^2, b. 60 cm^2, and c. 6 x 10^7 cm^2

3. Read the THEORY and PROCEDURE sections of this experiment.

4. Supply definitions for the KEY WORDS. The majority of these terms are discussed in the THEORY section.

5. Complete the PRELIMINARY REPORT. If you have difficulty, restudy the applicable portions of the THEORY section.

B. OBJECTIVES - You shall be able to:

1. Define and/or briefly discuss the KEY WORDS. This should aid your learning about adsorption.

2. Write the Freundlich and Langmuir equations in the form $y = mx + b$ and solve PROBLEMS 8-1 and 8-2.

3. Plot the data obtained in this experiment and evaluate the constants from the slope and intercept of the line.

4. Distinguish between chemisorption and physical adsorption given properties of each.

5. Apply the theoretical aspects of this experiment to environmental situations such as air and water pollution.

C. KEY WORDS: Supply a definition for each of the
following terms.

Activated charcoal

Adsorbate

Adsorbent

Adsorption vs. Absorption

Adsorption isotherm

Aliquot

Chemisorption

Freundlich isotherm

Langmuir isotherm

Physical adsorption

D. PRELIMINARY REPORT - Answer the following questions
prior to coming to the laboratory. You may be required to
turn this sheet in for grading or you may have a quiz prior
to performing the experiment.

1. Explain in writing the main differences between
chemisorption and physical adsorption as described in your
lecture textbook.

2. Write equations for the Freundlich equation and the
Langmuir equation. Explain in words the difference between
the two as discussed in your textbook and the THECRY section
of this experiment.

3. What is the reason for allowing the acetic acid and
charcoal mixture to remain in contact for about an hour?

4. Show the calculations for how you would dilute a 1.0 $\underline{N}$
acetic acid to 0.25 $\underline{N}$ in the same way as described in
this experiment.

E.   REFERENCES - These references are listed for those
students who may wish additional information.

1.   Daniels, et al., "Experimental Physical Chemistry,"
McGraw-Hill, New York, 1970, pp. 365 - 368.

2.   Salzberg, et al., "Physical Chemistry," Academic Press,
1969, pp. 133 - 134.

3.   Metz, C.R., "Theory and Problems of Physical Chemistry,"
McGraw-Hill, New York, 1976, pp. 192 - 194.

F.   APPARATUS AND CHEMICALS

Six 300 mL Erlenmeyer flasks, six 125 mL Erlenmeyer
flasks; two 50 mL burettes, one 100 mL volumetric flask, two
conical funnels (75 mm diameter), three pipettes (one each
of 5, 25 and 50 mL), and six 100 mL beakers, filter paper,
0.500 N standardized acetic acid, 0.100 N NaOH, phenolphtha-
lein, highly activated adsorbent charcoal, constant tempera-
ture bath is optional. (The NaOH should be standardized.
Granular charcoal works best.)

G.   INTRODUCTION

Adsorption describes the fact that various liquids,
gases or small particles of one substance tend to stick to
the surface of certain other solids without causing any
chemical change. Some solids have the ability to adsorb
large quantities of gases. Charcoal, because of its porous
nature, adsorbs most poisonous gases, hence its use in gas
masks. A more current application is the use of activated
charcoal to remove substances with objectionable odors from
water. A major industrial application of adsorption is in
removing impurities from sugar solutions. Finally, in the
softening of water with zeolites an exchange takes place in
which one ion is liberated from the resin while another is
adsorbed. In this experiment we will limit   our discus-
sions to only adsorption of a liquid on a solid surface.

H.   PURPOSE

1.   The purpose of this experiment is to study adsorption,
of acetic acid from an aqueous solution onto the surface of
activated charcoal, as a function of solute concentration
at constant temperature, and

2.   To determine whether that relationship may be described
by a mathematical equation.

I.   THEORY - ADSORPTION ON SOLID SURFACES

There are two distinct types of adsorption on solids as

well as many combinations in between these two. Chemisorp-
tion is the formation of a chemical bond between the surface
and the adsorbate. Typically, only one layer is formed. The
heats of chemisorption are on the order of 20 kcal/mole and
decrease with a greater area of surface coverage. Physical
adsorption, on the other hand, is much less specific and re-
sults from attractions, such as van der Waals attractions,
dipole-dipole attractions, etc., rather than bond formation.
Heats of physical adsorption are on the order of 10 kcal/mole
or less. More than one layer may be adsorbed, and sometimes
many layers are.

Adsorption is specific in nature, as its magnitude de-
pends upon the specific nature of both the adsorbate and the
adsorbent. When a porous solid, such as activated carbon,
is shaken with a dilute solution of acetic acid, an equilib-
rium is established between the amount adsorbed and the con-
centration of acid remaining in the solution, at a given
temperature. It is also found that the total amount of
material adsorbed varies directly with the mass of activated
charcoal used.

The amount of substance adsorbed per gram of solid depends
on the specific area of the solid, the equilibrium solute
concentration in the solution, the temperature, and the nature
of the molecules involved. From measurements at constant tem-
perature, one can obtain a plot of the amount of substance
adsorbed per gram of solid, versus the equilibrium solute
concentration. This is called an adsorption isotherm.

The relationship between the amount adsorbed and concen-
tration is not a linear one and depends on some function of
concentration raised to a fractional power. This relation-
ship is usually represented by the classical adsorption iso-
therm known as the Freundlich adsorption isotherm, which is
purely empirical in nature

$$x/m = kc^n \qquad (8-1)$$

where x is the mass of substance adsorbed, m the mass of
adsorbent, c the equilibrium concentration of the substance
adsorbed, and both k and n are constants.

This equation may be rewritten in the form of a straight
line:

$$\log (x/m) = n \log c + \log k. \qquad (8-2)$$

If $\log (x/m)$ is plotted against $\log c$, a straight line of
slope n and intercept $\log k$ should be obtained.

Another equation to be used is the Langmuir equation
based upon a theoretical consideration of the process of
adsorption. This equation may be written as:

$$\frac{x}{m} = \frac{k_1 c}{1 + k_2 c} \qquad \text{or} \qquad \frac{c}{x/m} = \frac{mc}{x} = \frac{k_2 c}{k_1} + \frac{1}{k_1} \qquad (8-3)$$

where k_1 and k_2 are constants and the other variables have the same meaning as before. For cases in which this equation represents the data, $c/(x/m)$ may be plotted as a linear function of c, and the constants, k_1 and k_2, evaluated from the slope k_2/k_1 and intercept $1/k_1$. The Langmuir equation differs from the Freundlich equation in that the adsorption approaches a finite limit as the concentration is increased.

For a limited range of concentrations it is frequently impossible to decide which of the two equations fits experimental data better. The Langmuir equation is somewhat better for adsorption of gases, while the Freundlich isotherm is somewhat better for the adsorption of a solute from a solution. There are, however, many exceptions, and many examples are known which fit neither of these two equations.

For multilayer adsorption there is no accepted theoretical isotherm. The Brunauer-Emmett-Teller (BET) semiempirical isotherm is most frequently used, especially in the determination of the surface area of powders and irregular solids.

See your lecture textbook for a discussion of the Gibbs equation which relates the effect of concentration of a solute to the surface tension of a solution. You may be performing a surface tension experiment as one of your next laboratory experiments.

As a reminder, the final normality of the acetic acid at equilibrium may be calculated by the reaction:

Normality x Volume = Normality x Volume.

The amount of acid adsorbed is $(c_0 - c)$ moles/liter which may be converted to grams (x) of acid adsorbed by the relation:

$(c_o - c)$ x M.W. of acid x Volume in liters.

J. EXPERIMENTAL PROCEDURE

1. Clean thoroughly with soap and water and dry the following pieces of apparatus: six 300 mL Erlenmeyer flasks, six 125 mL Erlenmeyer flasks, two 50 mL burettes, one 100 mL volumetric flask, two conical funnels (75 mm diamter), three pipettes (one each of 5, 25 and 50 mL), and six 100 mL beakers.

2. Accurately record the weights to $\pm$ 2 mg. Weigh onto glazed paper the following approximate amounts of charcoal: For flasks 1 and 2 - about 6 grams each; for flasks 3 and 4, about 4 grams each; for flask 5 - 2 grams; for flask 6 - 1 gram. Transfer the charcoal to the proper flasks and weigh the flazed paper accurately.

3. Into flask 1 pipette 50 mL of approximately 0.5N but standardized acetic acid, HAc. Note the approximate time at which this operation is performed and for each of the subsequent operations.

4. To each of the remaining flasks add exactly 50 mL of a more dilute solution of acetic acid, prepared as follows: Pipette 50 mL of 0.5 N HAc into the 100 mL volumetric flask. Fill the volumetric flask to the mark, mix the contents by successive inversions. If the volume decreases on mixing, refill to the mark and remix. Dry the 50 mL pipette by applying a vacuum. Pipette 50 mL of the resultant solution, approximately 0.25 N HAc, into flask 2. Rinse the pipette into volumetric flask and, repeating the steps above, prepare 100 mL of approximately 0.125 N HAc, 50 mL of which is to be pipetted into flask 3. In similar fashion prepare and pipette 50 mL each of the following acetic acid solutions into the remaining flasks: flask 4 - 0.0625 N; flask 5 - 0.03125 N; flask 6 - 0.01563 N. In each case note the approximate time at which the acetic acid solution is added to the charcoal. The contents of the flasks should be swirled periodically until equilibrium is reached.

5. About an hour after it was prepared, filter each mixture through fluted filter paper into a dry 100 mL beaker. Pipette the aliquot indicated as follows into a numbered 125 mL Erlenmeyer flask: flasks 1 and 2 - 5 mL; all remaining flasks 25 mL. It is important that the time between adding the charcoal and filtering the solution is about the same in each case.

6. Using the other burette titrate each aliquot with 0.1 N NaOH to the phenolphthalein end point. NOTE: There are no duplicate samples; so save original solutions until you finish calculations. In case an end-point is passed, you may back-titrate with the standardized HAc.

7. The amount of acetic acid adsorbed per gram of adsorbent is calculated and the Freundlich and Langmuir isotherms are tested by plotting as indicated in the CALCULATION section.

OPTION--(As determined by instructor.) (Additional adsorption measurements can be made at lower temperature, about 15° below room temperature, in order to establish the effect of temperature on adsorption. The slope of log k_1 versus the reciprocal of the absolute temperature, $1/T$, can be used to establish enthalpy and energy of adsorption and its magnitude may be used to characterize the adsorption process as physical or chemical.)

K. CALCULATIONS

1. Carry out the calculations indicated on the data sheet.

2. Plot x/m versus c.

3. Plot log (x/m) versus log c. Draw the best straight line through the points on the second plot and from this line determine the values of k and n.

4. Plot $c/(x/m)$ <u>versus</u> c. Again draw the best straight line through the points and from this line determine k_1 and k_2.

5. For the Freundlich isotherm, calculate the maximum error of the slope, n, and intercept, k, selecting points from the graph, and obtain the average error.

6. Work the PROBLEMS found at the end of this experiment and include them with your report.

L. SPECIAL INSTRUCTIONS

1. In the results and conclusion section explain the choice of the variables used to test graphically the application of the two theoretical isotherms, and comment on the use of each of these isotherms in relation to your data, i.e., which gives a better fit.

2. Comment on the problems of ensuring that thermodynamic equilibrium is reached in this experiment, and describe how the establishment can be verified.

3. The graphs should be placed at the end of your report. They should be labeled in accordance with the directions in UNIT I.

M. EXAMPLES AND PROBLEMS

EXAMPLE 8-1: The following data for the adsorption of
aqueous acetic acid on charcoal were obtained by Labowitz
(unpublished data)(Labowitz, L. C., and J. S. Arents,"Physical
Chemistry Problems and Solutions," Academic Press, 1969, p.176):

c_o, normality of HAc in solution before addition to charcoal	c, normality of HAc remaining in solution at equilibrium	m, grams of charcoal
0.503	0.434	3.96
0.252	0.202	3.94
0.126	0.0899	4.00
0.0628	0.0347	4.12
0.0314	0.0113	4.04
0.0157	0.00333	4.00

In all cases the volume of the solution in contact with the
charcoal was 200 mL. Show that these data fit the
Freundlich adsorption isotherm, $x/m = kc^n$ where x is
the number of grams of acetic acid adsorbed. Evaluate the
constants k and n.

Let x = number of grams of adsorbed CH_3COOH

$\quad\quad = (c_o-c)$ mole/liter x 0.200 liter x 60.0 g/mole

$\quad x/m = kc^n$

$\log \frac{x}{m} = n \log c + \log k$

Plot log(x/m) vs log c. You should get a straight line.

The intercept equals log k. The slope equals n.

c_o	c	x	x/m	log(x/m)	log c
0.503	0.434	0.828	0.209	-0.680	-0.362

The other five cases are treated similarly. Intercept for
log c = 0 is -0.552 = log k. log k = 9.448 - 10;

k = 0.28. Slope = 0.355 = n.

EXAMPLE 8-2: (Daniels et al., 1975, p. 268) The following
table gives the volume of nitrogen, V, in terms of the
number of mL nitrogen (reduced to $0^\circ C$ and 1 atm) absorbed
per gram of active carbon at $0^\circ C$ at a series of pressures:

P, torr	3.93	12.98	22.94	34.01	36.23
V, cm^3/g	0.987	3.04	5.08	7.04	10.31

Plot the data according to the Langmuir isotherm, and
determine the constants.

Using equation 8-32 on page 264 of Daniels (1975) gives:

$$1/V = 1/V_m + k^{\bullet}/V_m P$$

where V_m is the volume of a gas adsorbed when the entire surface is covered and $k = r/k$, where r is the rate of evaporation and k is a constant. V, is directly proportional to P at very low pressures where $(k/P) >> 1$. As the pressure is increased the volume adsorbed increases. However, most data in general, do not give a linear plot except at low pressures. Thus adsorption on solids is more complicated than the Langmuir theory indicates. Thus the above equation gives an intercept of 0.025 g/cm³,

$$V_m = 1/(0.025 \ g/cm^3) = 40 \ cm^3/g$$

$$slope = \frac{(1.00-0.025)g/cm^3}{0.25 \ Torr^{-1}}$$

$$= 3.9 \ g/cm^3 Torr = \frac{k^{\bullet}}{V_m} = \frac{k^{\bullet}}{40cm^3/g}$$

$$\underline{k = 156 \ Torr}$$

EXAMPLE 8-3: (Daniels et al., 1975, p. 268) The pressure of nitrogen required to cause the adsorption of 1.0 cm³/g (25°C, 1 atm) of gas on P-33 graphitized carbon black are 0.18 Torr at 77.5 K and 2.2 Torr at 90.1 K. Calculate the heat of adsorption at this fraction of surface coverage using the Clausius-Clapeyron equation.
■---------

Using equation 3-45 on page 99 of Daniels (1975) gives:

$$\ln \frac{P_2}{P_1} = \frac{\Delta H(T_2-T_1)}{RT_1 T_2}$$

$$\Delta H = \frac{RT_1 T_2 \ \ln(P_2/P_1)}{T_2 - T_1}$$

$$= \frac{(1.987 \ cal/K\text{-}mole) \ (77.5 \ K)(90.1 \ K)\ln(2.2/0.18}{(90.1 \ K - 77.5 \ K)(10^3 \ cal/kcal)}$$

$$= \underline{2.76 \ kcal/mole}$$

PROBLEM 8-1: Magnesium oxide adsorbs silica from water, and this adsorption follows the Freundlich equation as given in THEORY section and in EXAMPLE 8-1. Magnesium oxide may be used to remove silica from boiler scale. Make a log-log plot of the following data, and calculate the constants of the Freundlich equation. Calculate the parts per million, ppm, of magnesium oxide needed to reduce the residual silica to 2.9 ppm.

MgO, ppm		0	75	100	200
Residual SiO_2, ppm	26.2		9.2	6.2	1.0
SiO_2 removed, ppm	0		17.0	20.0	25.2

(Daniels, 1975, p. 269)   ANS: 143 ppm

PROBLEM 8-2: See if the following data fit a Langmuir
isotherm. If so, determine the constants, k_1 and k_2.

P(atm)	4.0	9.7	13.4	19.0	27.1
y	0.163	0.189	0.198	0.206	0.206

----------(KEMP, 1974, p. 11-90)

PROBLEM 8-3: (Daniels et al., 1975, p. 270) The adsorption
of ammonia on charcoal is studied at $30°C$ and $80°C$. It is
found that the pressure required to cause the adsorption of
a certain amount of NH_3 per gram of charcoal is 106 Torr at
$30°C$ and 560 Torr at $80°C$. Calculate the heat of adsorption
using the Clausius-Clapeyron equation.

N. DATA AND RESULTS--Experiment 8

		1	2	3	4	5	6
1.	Flask number						
2.	Wt charcoal + paper						
3.	Wt paper						
4.	Wt charcoal (m)						
5.	Vol HAc soln added						
6.	Orig $\underline{N}$ of HAc (c_o)						
7.	Aliquot taken						
8.	Burette reading final						
9.	Burette reading initial						
10.	Volume NaOH req'd						
11.	Final $\underline{N}$ of HAc (c)						
12.	$c_o - c$						
13.	Wt of HAc adsorbed (x)						
14.	x/m						
15.	Log x/m						
16.	Log c						
17.	k						
18.	n						
19.	cm/x						
20.	k_2/k_1						
21.	$1/k_1$						

A copy of this sheet with your data for items 2, 3, and 5
through 9 should be filled with your instructor before the
end of the laboratory period.

APPENDIX H

SURFACE TENSION

APPENDIX H

EXPERIMENT 9: SURFACE TENSION

A. STUDY GUIDE AND REVIEW ASSIGNMENT

1. Read the appropriate sections of your lecture textbook
to obtain an overview of surface tension. Do this prior
to coming to lab.

2. Read the THEORY and PROCEDURE sections of this
experiment prior to coming to lab.

3. Supply definitions for the KEY WORDS. The majority of
these are discussed in the THEORY section.

4. Complete the PRELIMINARY REPORT of this experiment
prior to lab.

5. You will be using the Du Noüy tensiometer method in this
experiment. Check with the instructor for a copy of
instructions on using the tensiometer.

6. Be prepared to discuss any questions concerning the
THEORY and tensiometer operation with your instructor at
the beginning of the lab period.

7. NOTE: The symbol used for density in this experiment
is d. The symbol d can be replaced by ρ throughout.

B. OBJECTIVES - You shall be able to:

1. Define and/or briefly discuss the KEY WORDS on this
page.

2. Apply the determination of the surface tension of
liquids by the tensiometer method (Experiment 9).

3. Calculate the surface tension of a liquid using the
capillary rise method (EXAMPLES AND PROBLEMS).

4. Explain the four methods used in the determination of
surface tension.

C. KEY WORDS: (Supply equations where possible.)

Bubble pressure method

Capillary action

Density, d

Drop weight method

Eotvos equation

Gibbs' equation

Interfacial tension

Non-associating liquids

Ramsay-Shields equation

Surface tension, γ

Tensiometer

Torsion

Wetting

Work of Adhesion

D.   PRELIMINARY REPORT - Complete this self-test prior to beginning your laboratory experiment on surface tension.

1.   Why is it important for you to have extremely clean glassware in this experiment?

2.   How does surface tension change with increasing temperature?

3.   Can you calculate the critical temperature of a substance using surface tension data?   How?

4.   What is the purpose of measuring the surface tension of various solutions of $CaCl_2$?

E.   REFERENCES and SUPPLEMENTARY READING - These references are listed for those students who may wish additional information.

1.   Daniels, F., and R. A. Alberty, "Physical Chemistry," John Wiley, 1975, pp. 252-261.

2. Kemp, M. K., "Physical Chemistry for Engineering and the Physical Science," Marcel Dekker, 1974, pp. 14.51-14.68.

3. Kittsley, S. L., "Physical Chemistry," Barnes & Noble, 1969, pp. 24-27.

4. Schaum, B. S., "College Physics," McGraw-Hill, 1961, pp. 108-1110.

5. Wright, F. J., <u>Journal of Applied Chemistry</u>, 1961, pp. 193-196.

F. APPARATUS AND CHEMICALS

DuNoüy tensiometer (See Figure 9-1), Petri dish, distilled water, benzene, chloroform, n-octane, 6 $\underline{M}$ CaCl$_2$ solution, detergent solution, two 10 mL graduate cylinders, small flasks (125 mL), corks for flasks.
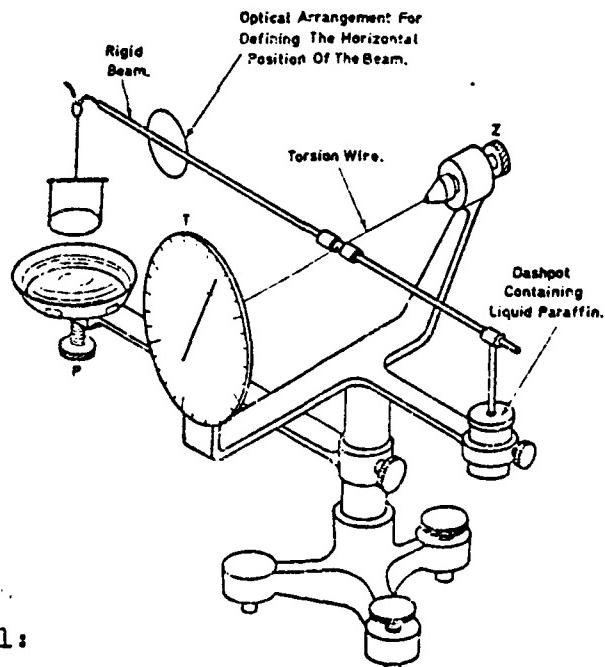
FIGURE 9-1:

The Du Noüy tensiometer. Suitable dimensions for the ring are $4\pi R = 8.0$ cm, $R/r = 40$; R and r are the radii of the ring and the wire, respectively. The dish should be at least 8 cm in diameter. The instrument should be placed in good light and still air; it should also be free from moisture. (Daniels et al., 1956, p. 56)

G. PURPOSE

The object of this experiment is the determination of
the surface tension of pure liquids and of solutions.

H. THEORY

The origin of surface phenomena is the imbalance of forces
on the molecules of the liquid. In the interior of a liquid
each molecule is completely surrounded by molecules which
leads to a balanced or symmetrical force about the center of
the molecule. This is not the case for a molecule on the
surface. A surface molecule is attracted to molecules
beneath and adjacent to it. However, there are no molecules
above it to balance the forces beneath it. The resulting
imbalance of forces results in a net inward force which causes
the liquid to behave as though it were surrounded by an invis-
ible membrane. The liquid tends to assume that shape which
has the smallest possible surface area (i.e., a sphere). This
phenomena is referred to as surface tension.
The surface, or interface, where tension exists is between
the liquid and its saturated vapor in air. A tension may also
exist at the interface between immiscible liquids; this is
commonly called the interfacial tension. Interfacial tension
may be calculated in the same manner as described in this
experiment.
Some observations you may have made are explained by the
surface tension of the liquid. Some of these are:

1. a "water bug" walks on the water without penetrating the
surface

2. water rises in a capillary tube, mercury falls

3. raindrops are spherical

4. a steel needle can float on water.

The thermodynamic explanation of surface tension is the
tendency of a system to achieve the lowest free energy. Thus
surface tension is the result of a system trying to minimize
its surface area.
Any attempt to increase the surface area of a system will
require an input of work to increase the free energy of the
system. The easiest way to derive the equations needed to
describe surface tension is to consider a thin film of sub-
stance floating on the surface of another liquid. Refer to
further discussion of this topic in your lecture textbook.

MEASUREMENT

There are many methods that can be used to determine the
surface tension of a liquid. You will use the tensiometer

method in this experiment. Three other methods are capillary rise, drop weight, and bubble pressure. The simplest and most accurate is the capillary method. Therefore, we will discuss this method more thoroughly than the other three methods.

Most liquids (e.g., water) wet the walls of a glass capillary tube, that is, the liquid adherring to the walls pulls a column of the liquid up. This causes liquids which wet the walls to rise in a capillary tube. If the liquid does not wet the walls (e.g., mercury) the liquid is depressed. The best way to measure the surface tension is by measuring the height the liquid that rises in a capillary tube of known radius.

A capillary tube of known radius, r, is immersed in a liquid of density, d. Assuming that the liquid wets the walls, the liquid will rise until the force of surface tension which tends to pull the liquid up is just counterbalanced by the force tending to pull the liquid down. The height to which the liquid rises above the surface is represented by h.

The force tending to pull the liquid down is $\pi r^2 hdg$, in which g is the acceleration due to gravity and where πr^2 is the area of the surface. The force tending to pull the liquid up is $2\pi r \gamma \cos \theta$, in which γ is the surface tension of the liquid and θ is the angle of contact between the surface of the liquid and the walls of the tube. Thus

$$\pi r^2 hdg = 2\pi r \gamma \cos \theta$$

or:

$$\gamma = \frac{hdgr}{2\cos\theta}.$$ (9-1)

Since θ is approximately zero for most liquids, $\cos \theta = 1$. Then:

$$\gamma = \frac{hdgr}{2}.$$ (9-2)

If h and r are in cm., d in grams/cubic centimeter, and g in cm/sec^2, then surface tension has the units of dynes/cm. Thus if you are given the capillary radius, the density of the liquid and the height of the rise, you can quickly determine the surface tension of a liquid.

For very precise work the volume of liquid under the meniscus must be included. Also a correction factor for the density of the gas above the liquid must be applied. The modified equation takes the form

$$\gamma = \frac{(h + r/3)\ (d_1 - d_g)rg}{2}$$ (9-3)

(See EXAMPLES AND PROBLEMS)

SURFACE TENSION AND TEMPERATURE

The original linear relationship for the dependence of surface tension on temperature was given by Eotvos:

$$- \frac{\partial}{\partial T}(\gamma (\frac{M}{d})^{2/3}) = k \quad .$$

where M is the molecular weight and k is the Eotvos constant which equals 2.12 for most <u>non-associating liquids</u>. The negative sign indicates that molar surface energy decreases with increasing temperature.

This relationship was modified by Ramsay-Shields to give:

$$\gamma = (\frac{M}{d})^{2/3} = k(T_c - T - 6) \tag{9-4}$$

where T_c = critical temperature and T = absolute temperature of liquid both in degrees Kelvin. Thus surface tension decreases with increasing temperature. At the critical temperature you should recognize that the surface tension goes to zero.

(a) CAPILLARY RISE   (b) RING

(c) DROP WEIGHT   (d) BUBBLE PRESSURE
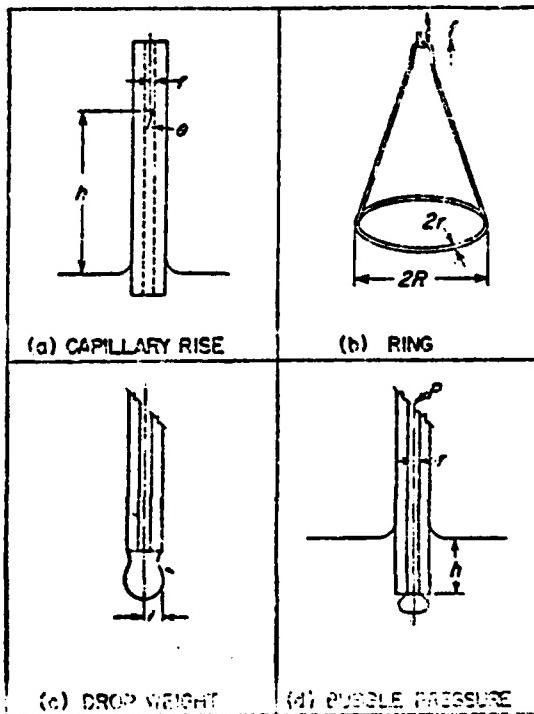
(Daniels et al. 1956, p. 52)

FIGURE 9-2: Principles of four-surface-tension methods.

OTHER METHODS

The principle of operation of the capillary-rise method already discussed is illustrated in Figure 9-2 along with the other three principles of operation now to be discussed.

In the drop-weight method, a drop forms at the end of a tube assumed to equal the outside perimeter of the tube, $2\pi r$. When detached the force downward on the drop is mg which is equal to the force acting upward, $2\pi r^2\gamma$, giving

$$m_i g = 2\pi r\gamma$$

where m_i is the mass of an "ideal" drop. A more convenient equation is

$$\gamma = \frac{mgF'}{r} \qquad (9-5)$$

where F' is an empirically determined function of v'/r^3 and v' is the actual volume of the drop.

In the bubble-pressure method, a gas bubble is forced through a capillary of known radius. To form this bubble in a liquid, the pressure inside the bubble must be greater than the pressure outside the bubble. The relationship between the radius and pressure is as follows:

$$p_i - p_o = 2\gamma/r \qquad (9-6)$$

where p_i is the inside pressure, p_o is the outside pressure, and r, is the radius of curvature of the surface. The excess pressure on the inside of the bubble is needed to balance the force of surface tension.

In this experiment you will be calculating surface tension by means of the Du Nouy tensiometer method which measures the force needed to expand a surface (See Figure 9-3). A horizontal planar ring immersed in the liquid is pulled through the surface by a force supplied by a torsion balance. The surface tension is the applied force divided by the length of contact between the wire and the surface. The length of contact depends upon the thickness and the diameter of the ring. To a close approximation, the ring, just before it breaks through holds up a hollow cylinder of liquid. The perimeter of contact is $2(2\pi r)$ where r is the radius of the ring, since contact is made at both the inner and outer edges of the ring. For a thick wire, however, the circumference of the inner and outer ring are not equal. The average perimeter is therefore $4\pi(r + r')/2$ where r and r' are the inner and outer radii respectively. Thus surface tension is given by

$$\gamma = \frac{f\ F}{4\pi R} \qquad (9-7)$$

where f is the maximum force registered on the torsion-balance scale, F is the correction factor due to the shape

of liquid held up and the ring dimensions, and R is the mean radius of the ring. The shape is a function of R^3/V and r/r', where V is the volume of liquid held up. F varies between 0.75 and 1.02 and may be approximated as 1. If the ring is distorted or bent out of a plane, the applied force is no longer equal to the surface tension, and the measurements are not valid.

The tensiometer is rapid and accurate for pure liquids. For solutions the results are accurate enough for student use; but not for research. For very precise work the surface tensions computed from the readings of the tensiometer must be corrected as outlined above. The commercial instrument is equipped with a platinum-iridium ring of standard dimensions for which the dial has been calibrated to read directly in dynes per centimeter. The ring may be quickly and easily cleaned by flaming, avoiding the laborius purification required by some of the other methods.

I. EXPERIMENTAL PROCEDURE

In this experiment you will compare the force required to pull a platinum ring away from the surface of water with that required when any one of several aqueous solutions is substituted for water. Similarly you will compare the force required when benzene is under test to that required in the case where another organic liquid is employed.

The force is measured by the torsion in a wire. The platinum ring is suspended from a metal arm which is attached at right angles to the wire under torsion. As the wire is twisted, a pointer attached to one of its ends moves over a circular scale; the scale can be calibrated directly in terms of surface tension by the use of liquids of known surface tension.

Simplified du Nouy tensiometer. (Used by permission of The Central Scientific Co.)

Cross section of ring (greatly magnified)

Breaking line

Liquid

Ring holding up surface.
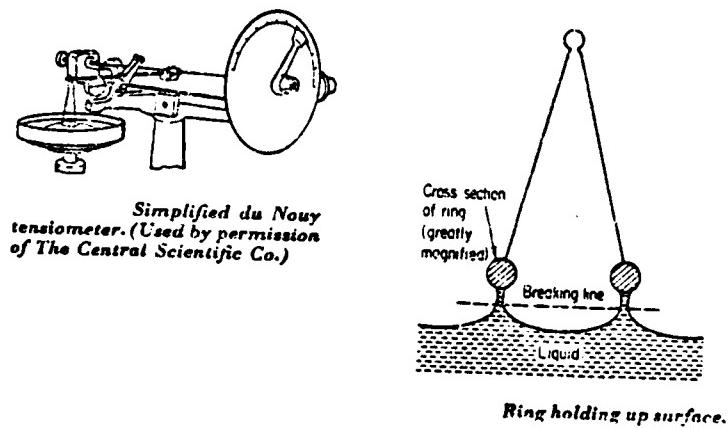
FIGURE 9-3: (Crockford & Nowell, 1956, p. 60)

The type of method described in the previous two paragraphs is a relative method; data determined by such a method depend upon assumed values of the properties of the reference substances.

Cleanliness - Perhaps no other measurement you will make in the laboratory is so sensitive to impurities as surface and interfacial tension. Therefore you must be certain the chemicals used are pure and the vessels and instruments used are clean.

All determinations are to be performed at room temperature. Solutions and equipment should be at the same temperature.

1. Check out a Du Nouy tensiometer and other special equipment for Experiment 9.

2. Clean the platinum ring in hot chromic acid cleaning solution. CAUTION: hot cleaning solution should be handled with great care. Naturally, you will be wearing your safety glasses. Rinse the ring in distilled water. Dry the ring by passing it several times through a non-luminous Bunsen flame. DO NOT heat the ring for more than a few seconds.

3. Hang the clean ring on the tensiometer hook. Turn the smaller of the two knobs which are coaxial with the wire until the slack in the wire is taken up; the smaller knob should be turned until a sudden increase is felt in the resistance to rotation.

4. Turn the knob at the right of the dial until the pointer is at zero.

5. Turn the larger of the two knobs which are coaxial with the wire until the tensiometer arm is horizontal. (One type of tensiometer is equipped with a pointer and index which should be brought into coincidence. Another type is not so equipped and its arm must be brought close to the arm rest; care must be taken to see that the arm does not touch the arm rest, but the gap between the two should be very small.)

6. Clean the Petri dish; use laboratory soap and a small brush. Rinse the dish under tap water until all traces of the soap have been washed away; then, rinse the dish with several portions of distilled water.

7. Fill the Petri dish half full of distilled water. Place the dish on the movable table on the tensiometer. Record the room temperature.

8. Raise the movable table a few millimeters past the point where the ring touches the surface of the water. Be sure that the ring is completely immersed in and wet by the water.

9. Start lowering the movable table; when the arm falls slightly below the position established at the end of paragraph 5, turn the knob to the right of the dial so as to counteract this downward motion. As the lowering of the movable table is continued, maintain the tensiometer arm at its zero position (i.e., horizontal; with pointer and index mark in coincidence, or with the arm slightly above the arm rest, as the case may be.)

10. When the ring is torn from the surface of the water, the reading of the dial is proportional to the surface tension of the water. Repeat steps 8 through 9 twice. (In the calculations for this experiment, the mean of these three readings will be used.)

11. Repeat steps 3 and 6 through 10 for each of the following liquids: benzene, chloroform, n-octane. Record the temperature.

12. Prepare the following solutions and determine their surface tensions as in 11:

Solution No.	1	2	3	4	5
mL 6 M $CaCl_2$ soln.	2	4	6	8	10
mL water	8	6	4	2	0

13. Fill the Petri dish half full of dilute detergent solution. Determine the surface tension of the solution as quickly as possible. Count from the moment the dish is filled; record the time at which the film breaks in the surface tension determination. Repeat the determination at such intervals that film breaks occur approximately 2, 5, 10, and 15 minutes after the dish was filled. In each case, be sure to record the time when the film breaks. Between the readings, the ring should be kept immersed in the detergent solution.

J. CALCULATIONS

Calculate the surface tensions of the several $CaCl_2$ solutions and of the detergent solution; use the water calibration of the apparatus. Using the benzene calibration, calculate the surface tensions of chloroform and n-octane.

For the $CaCl_2$ solutions plot the observed surface tension verus molarity. For the detergent solution plot observed surface tension versus time of film breakage.

QUESTIONS

1. How does temperature affect surface tension?

2. What is the value of the surface tension of benzene at the critical temperature?

3. What is the origin of surface tension?

4. Explain the meaning of the units used to measure surface tension.

5. Upon what principle does each of the following methods for surface tension determination depend?

    a. Maximum bubble pressure method
    b. Drop-weight method
    c. Capillary rise method.

6. What is an absolute method for surface tension determination? (See THEORY and EXAMPLES AND PROBLEMS sections).

7. If water had a negative surface tension could it rain?

K. EXAMPLES AND PROBLEMS

EXAMPLE 9-1: (Kemp, 1974, p. 14-56) Water (γ = 0.07275 N/m) at 20 °C is observed to rise 0.030 m in a capillary. Methanol at the same temperature and in the same capillary rises to a height of 0.012 m. What is the surface tension of methanol?

d^{20} methanol = 791.4 kg/m^3, d^{20} H$_2$O = 998.2 kg/m^3

The data for water can be used to find the capillary radius. From Equation 9-2 and assuming that θ = 0:

$$r = \frac{2\gamma}{dgh} = \frac{(2)(0.07275 \ N/m)}{(998.2 \ kg/m^3)(9.80 \ m/s^2)(0.030 \ m)}$$

$$= 4.96 \times 10^{-4} m \ (=0.496 \ mm)$$

Then, for methanol,

$$\gamma = \frac{rdgh}{2}$$

$$= \frac{(4.96 \times 10^{-4} m)(791.4 \ kg/m^3)(9.8 \ m/s^2)(0.012 \ m)}{2}$$

$$= 0.023 \ N/m.$$

EXAMPLE 9-2: (Kemp, 1974, p. 14-67) If, in a surface tension experiment using a capillary tube, the angle θ was actually 10° instead of 0°, what percent error would this cause if you assumed θ = 0° in all your calculations? (Assume the only error is in θ.)

Using Equation 9-1: $\gamma = \frac{rdgh}{2\cos \theta}$

$$\ln \gamma = \ln r + \ln d + \ln g + \ln h - \ln 2 - \ln \cos \theta$$

$$\frac{\Delta \gamma}{\gamma} = \cancel{\frac{\Delta r}{r}}^{0} + \cancel{\frac{\Delta d}{d}}^{0} + \cancel{\frac{\Delta g}{g}}^{0} + \cancel{\frac{\Delta h}{h}}^{0} + \cancel{\frac{\Delta 2}{2}}^{0} + \frac{\Delta \cos \theta}{\cos \theta}$$

$\cos 0$ = 1, $\cos 10$ = 0.984, $\Delta \cos \theta$ = 0.015

$$\frac{\Delta \gamma}{\gamma} = \frac{\Delta \cos \theta}{\cos \theta} = \frac{0.015}{1} = 0.015 \ --- \ 1.5\%$$

EXAMPLE 9-3: (Schaum, 1961, p. 109) Pressure due to surface tension: Surface tension causes the pressure inside a drop of liquid or a bubble filled with gas to be greater than the pressure outside.

    1. In a spherical drop: $p = 2\gamma/r$

    2. In a spherical bubble which is filled with gas:
$p = 4\gamma/r$; where γ = surface tension of the liquid,
r = radius of drop or bubble, p = pressure inside - pressure
outside drop or bubble.

Determine the work in in-lb required to increase the
diameter of a spherical soap bubble from 2 in. to 6 in., if
the surface tension is 0.0028 lb/ft.

The bubble has two surfaces, inside and outside. Surface
area of sphere = $4\pi r^2$.

$$\text{Work (in-lb)} = 2 \times 4\pi(3^2 - 1^2)\text{in}^2(.0028/12 \text{ lb/in})$$

$$= \underline{0.047 \text{ in-lb}}.$$

EXAMPLE 9-4: (Schaum, College Physics, 1961, p. 109)
Compute the pressure (due to surface tension) within a soap
bubble of diameter 0.8 inches. Surface tension is
0.0024 lb/ft.

The film has two surfaces, inside and outside.

$$p = \frac{2\gamma}{r} + \frac{2\gamma}{r} = \frac{4\gamma}{r} = \frac{4 \times 0.0024 \text{ lb/ft}}{0.4/12 \text{ ft}} = 0.29 \text{ lb/ft}^2.$$

PROBLEM 9-1: (Schaum, 1961, p. 109) A horizontal loop of
platinum wire of perimeter 16 cm is lowered into an alcohol
sample. The added force (due to surface tension) required
to pull the loop out of the liquid is 772 dynes. Find the
surface tension of the alcohol.

                                          ANS: 24 dynes/cm

PROBLEM 9-2: (Kittsley, 1969, p. 25) Acetone rises 5.12 cm
in a capillary tube which has a radius of 0.0117 cm. The
density of acetone is 0.790 g/cm^3. Calculate the surface
tension of acetone.

                                       ANS: 23.2 dynes/cm

PROBLEM 9-3: (Kemp, 1974, p. 14-67) At $20°C$ a sample of acetone is observed to rise to a height of 2.03×10^{-2} m. Use Equation 9-3 to find the height ethanol would rise to in the same capillary at the same temperature.

ANS: h = 0.0192 m

PROBLEM 9-4: (Kittsley, 1969, p. 25) Acetone has a surface tension of 23.7 dynes/cm at $20°C$ and a density of 0.792 g/cm^3; it rises 1.5 cm in a certain capillary. What is the radius of the capillary?

ANS: r = 0.0407 cm

PRCBLEM 9-5: Using the data in Problem 4, calculate the critical temperature of acetone, CH_3COCH_3, assuming the Eotvos constant of acetone is 1.9.

(Kittsley, 1969, p. 27)   ANS: T_c = 516 K

EXPERIMENT IX

Name: _____ Date: _____

L. Data and Results

    A. Water.   Temperature of water: _____ $^{\circ}$C

         1. _____   Surface tension of water (Tables) _____

         2. _____   dynes/cm

         3. _____   mean reading: _____

    B. Organic liquids.   Temperature of benzene: _____ $^{\circ}$C

	Benzene	Chloroform	n-Octane
1.	_____	_____	_____
2.	_____	_____	_____
3.	_____	_____	_____
mean:	_____	_____	_____

Surface tension of benzene (Tables): _____ dynes/cm

Surface tension of liquid (calc): _____ : _____

    C. $CaCl_2$ solutions

Solution No. 1	2	3	4	5
1. _____	_____	_____	_____	_____
2. _____	_____	_____	_____	_____
3. _____	_____	_____	_____	_____
mean: _____	_____	_____	_____	_____
Sur. Tens: _____	_____	_____	_____	_____

    D. Detergent solutions.

         Time: _____   Reading: _____

                _____   _____

                _____   _____

                _____   _____

                _____   _____

File a copy of your data with the instructor before leaving lab.

APPENDIX I

BINARY SOLID-LIQUID PHASE DIAGRAM

APPENDIX I

EXPERIMENT 10: BINARY SOLID-LIQUID PHASE DIAGRAM

A. STUDY GUIDE

1. Review the section of your lecture textbook concerned with the theory of Two-Component systems.

2. Read the THEORY and PROCEDURE sections of this experiment.

3. Supply definitions for the KEY WORDS. The majority of these terms are discussed in the THEORY section.

4. Complete the PRELIMINARY REPORT.

5. Be prepared to draw a typical cooling curve for a pure substance and for a binary mixture.

6. Explain how to interpret a cooling curve. How can data from cooling curves be used to construct a phase diagram?

7. Be able to state the phase rule and to know how to apply it to a binary system. What do F, C, and P symbolize?

8. Be prepared to draw and discuss a simple eutectic diagram.

B. OBJECTIVES - You shall be able to:

1. Define and/or briefly discuss the KEY WORDS.

2. State and apply the Gibbs Phase Rule.

3. Use cooling curve data to produce simple two-component solid-liquid phase diagrams or vice versa.

4. Label the regions in any two-component phase diagram you are given.

C. KEY WORDS

Components

Degrees of freedom

Eutectic

Gibbs Phase rule

Intensive variable

Phase

Phase diagram

Peritectic

D. PRELIMINARY REPORT - Answer the following prior to coming to the laboratory. You may be required to turn this sheet in for grading or you may have a quiz prior to performing the experiment.

1. State the phase rule.

2. Define F, C, and P.

3. Draw and discuss a simple eutectic diagram.

4. From the phase rule deduce the maximum number of degrees of freedom of a two-component system.

E. REFERENCES

1. Daniels, F., and R. A. Alberty, "Physical Chemistry," 1975, pp. 125-127.

2. Kemp, M. K., "Physical Chemistry for Engineering and the Physical Science," Marcel Dekker, 1974, pp. 13.22-13.41.

3. Illustrated World of Science Encyclopedia, Volume II, "Two-Component Systems," 1971, p. 139.

F. THEORY

In this experiment the solid-liquid equilibria in the system Naphthalene-Biphenyl will be studied. The phase diagram will be constructed using information obtained from cooling curves of mixtures of the two compounds.

The Gibbs Phase Rule is $F = C - P + 2$, where F is the variance (number of degrees of freedom), C the number of components, and P the number of phases in equilibrium. F is equal to the difference between the total number of intensive variables required to describe the system in equilibrium and the number that cannot be independently varied.

When no artificial restrictions are placed on their values, the number 2 in the formula above is taken to represent the two independent variables T and P. If either or both of these are restricted to particular values, the variance is correspondingly reduced. If, in addition to T and P some other independent intensive variable, such as gravitational or electric field, must be considered, the number in the phase rule becomes 3.

The naphthalene-biphenyl system will be studied over a range of temperatures but at constant pressure; for this situation the phase rule becomes

$$F = C - P + 1 = 2 - P + 1 = 3 - P.$$

The maximum number of phases which can coexist in the system to be studied at constant pressure is 3. Since an actual system can never have fewer than one phase, the maximum value of F is 2. A variance of 2 can be represented graphically on a two-dimensional plot. For the situation presented by the system to be studied the natural variables are the temperature and the composition.

G. PROCEDURE #1

1. Weigh approximately 16 g of pure biphenyl to the nearest 10 mg. Place the biphenyl in a clean, dry 20 mm Pyrex test-tube fitted with a rubber sleeve and melt it carefully over a small Bunsen flame.

2. Place the sample-containing tube into the wider test-tube provided for the experiment and clamp this in a large beaker of ice water so that it is well immersed.

3. Insert a partial immersion thermometer into the molten biphenyl and, while stirring gently and continuously, record the temperature to the nearest $0.1°$ at thirty second intervals, until the temperature is two degrees below the freezing point.

4. Weigh <u>approximately</u> 2 g of pure naphthalene to the nearest 10 mg and add to the sample tube; melt the mixture of crystals. The molten mixture may be cooled to about 60°C under the tap before placing the sample tube in the larger test-tube; be sure to dry the outside of the sample tube. CLAMP THE LARGER TEST-TUBE IN AIR, NOT ICE-WATER. This mixture will freeze high enough that no ice-water cooling is needed.

5. If no crystals have appeared, begin recording the temperature at thirty second intervals. (If crystals have appeared the sample was cooled too much and must be remelted.) Note the time at which the first crystals appear and note any behavior which would indicate under cooling.

6. Repeat steps 4 and 5 four more times; i.e. by adding 2 g Naphthalene each time until a total of 10 g of naphthalene have been added to the biphenyl. IN THESE RUNS CLAMP THE LARGER TEST-TUBE IN ICE-WATER AS IN STEP 2. This will speed the process.

7. Empty the mixture of crystals into the waste jar. Clean the tube with toluene.

PROCEDURE #2

8. Determine the melting point of a 16 g sample of pure naphthlene; follow the procedure in steps 1 and 2 and 3.

9. Weigh out approximately 6 g of biphenyl to the nearest 10 mg; add it to the naphthalene. Melt the mixture of crystals and precool to a temperature no lower than 70°; then proceed as in steps 4 and 5 adding 3 g biphenyl each time until a total of 18 g biphenyl have been added.

H. CALCULATIONS

1. For each sample, plot the temperature (as ordinate) vs. time. These cooling curves will be used to construct the phase diagram for the system. You will have notes from the instructor's discussion on the interpretation of cooling curves; this information may be extended by reference to your text. For the first two curves obtained show what phases appear or disappear at each break or halt of the curve.

2. Calculate the composition in mole fractions of each of the mixtures employed. Plot the temperatures at which breaks or halts occur in the cooling curves (as ordinates) vs. mole fraction of either component (as abscissa). Draw smooth curves through the points to get the phase diagram.

3. In constructing the phase diagram, label all points and regions. Determine the composition and temperature of any eutectic or peritectic points.

4. Include a _discussion_ of the possible source of errors.

I. DATA AND RESULTS

1. Cooling data-Indicate mixture number (1-7) or (8-9).

Time (Min)	Temp ($^\circ$C)	Time	Temp	Time	Temp	Time	Temp
___	___	___	___	___	___	___	___
___	___	___	___	___	___	___	___
___	___	___	___	___	___	___	___
___	___	___	___	___	___	___	___
___	___	___	___	___	___	___	___
___	___	___	___	___	___	___	___
___	___	___	___	___	___	___	___
___	___	___	___	___	___	___	___
___	___	___	___	___	___	___	___
___	___	___	___	___	___	___	___
___	___	___	___	___	___	___	___
___	___	___	___	___	___	___	___
___	___	___	___	___	___	___	___
___	___	___	___	___	___	___	___
___	___	___	___	___	___	___	___
___	___	___	___	___	___	___	___
___	___	___	___	___	___	___	___
___	___	___	___	___	___	___	___

2. Composition and other data

| Mix. No.	Wt. in grams Naphth.	Biphen.	Mole Fractions Naphth.	Biphen.	Temp. of Breaks or Halts	
——	——	——	——	——	——	——
——	——	——	——	——	——	——
——	——	——	——	——	——	——
——	——	——	——	——	——	——
——	——	——	——	——	——	——
——	——	——	——	——	——	——
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——	——	——	——	——	——	——
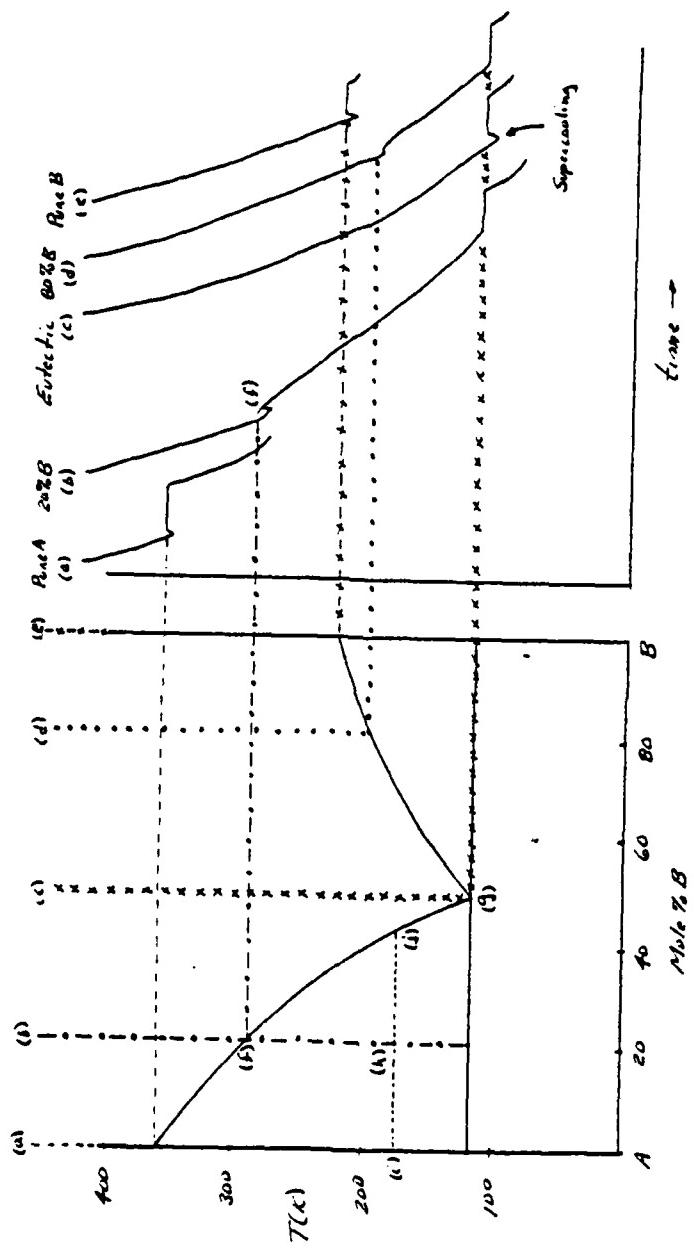
FIGURE 10-1: Cooling Curves for a Simple Eutectic System (Kemp, 1975, p. 13-25)

J. EXAMPLES AND PROBLEMS

EXAMPLE 10-1: The following data were obtained by thermal analysis of melts in a magnesium-siliconsystem (R. Vogel, Z. anorg. allgem chem. 61, 46, 1909).

Composition (weight per cent Mg)	Break (t°C)	Temperature Halt (t°C)
0	---	1420
15	1290	950
30	1150	950
43	---	950
55	1070	950
63	---	1102
80	1000	640
97	---	640
100	---	651

Construct a phase diagram for a magnesium-silicon system and determine the formula of the compound formed.
--------During thermal analysis a break appears on the cooling curve if the number of phases in the system changes. When cooling the melt the break on the cooling curve gives the temperature at which the first crystals of the precipited solid appear, i.e., the attaining of the equilibrium curve. The temperature halt gives the melting points of the pure constituents, eutectic mixtures and compounds, which are formed by the two components.

By plotting the breakpoints and the temperature halts against the composition we obtain points on the equilibrium curve of the phase diagram as shown.

When a compound is formed, it is represented in the phase diagram by a maximum on the equilibrium curve between the liquid and solid phases. In the figure the maximum corresponds to a mixture containing 63 weight per cent of magnesium. The ratio of the atoms of magnesium and silicon in the compound is

M.W. Mg = 24.3
M.W. Si = 28.1

$$\frac{Mg}{Si} = \frac{63/24.3}{37/28.1} = \frac{1.97}{1} = \frac{2}{1}$$

The compound of magnesium and silicon thus has the formula Mg_2Si.
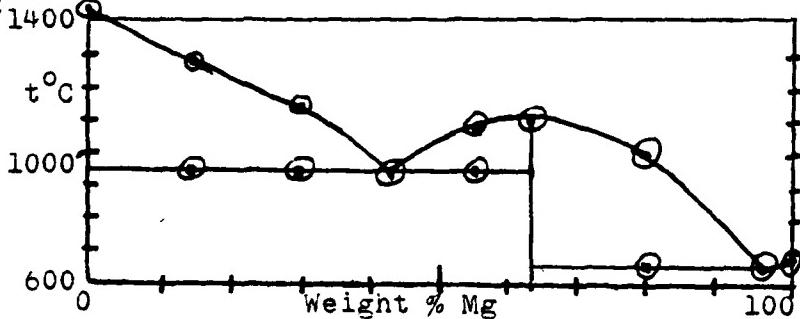
PROBLEM 10-1: Indicate precisely the conditions under which the formula $P + F = C + 2$ is valid.

PROBLEM 10-2: (Daniels, 1975, p. 142) The phase diagram formagnesium-copper at constant pressure shows that two compounds are formed: $MgCu_2$ which melts at $800^{\circ}C$, and Mg_2Cu, which melts at $580^{\circ}C$. Copper melts at $1085^{\circ}C$, and Mg at $648^{\circ}C$. The three eutectics are at 9.4% by weight Mg ($680^{\circ}C$), 34% by weight Mg ($560^{\circ}C$), and 65% by weight Mg ($380^{\circ}C$). Construct the phase diagram. State the variance for each area and eutectic point.

ANS: In the liquid region $v=2$, in the two-phase regions $v=1$, and at the eutectic points $v=0$.

PROBLEM 10-3: (Daniels, 1975, p. 145) The following cooling curves have been found for the system antimony-cadmium:

Cd, % by weight	0	20	37.5	47.5	50	58	70	93	100
First break , $^{\circ}C$	--	550	461	--	419	--	400	--	--
Continuing constant Temp, $^{\circ}C$	630	410	410	410	410	439	295	295	321

Construct a phase diagram, assuming that no breaks other than these actually occur in any cooling curve. Label the diagram completely, and give the formula of any compound formed. State the variance in each area and at each eutectic point.

APPENDIX J

RATE AND ORDER OF A CHEMICAL REACTION

APPENDIX J

EXPERIMENT 11: RATE AND ORDER OF A CHEMICAL REACTION

A. STUDY GUIDE

1. Read the appropriate sections of your lecture textbook
to obtain an overview of rate and order determinations in
kinetics. Do this prior to coming to lab.

2. Read the THEORY and PROCEDURE sections of this
experiment prior to coming to lab.

3. Supply definitions for the KEY WORDS. The majority of
these are discussed in your lecture textbook.

4. Complete the PRELIMINARY REPORT of this experiment
prior to lab.

B. OBJECTIVES - You shall be able to:

1. Define and/or briefly discuss the KEY WORDS for this
experiment.

2. Determine the specific rate constant for the
saponification of methyl acetate.

3. Fit your data to the appropriate rate law and determine
the rate constant.

4. Discuss how the kinetics of a reaction can be followed
by a conductometric method.

C. KEY WORDS: (Supply equations where possible.)

Conductometric

Half-time

Hydrolysis, saponification

Kinetics

Order
    1st order
    2nd order

Rate

Specific (or reaction) rate constant

D. PRELIMIMINARY REPORT - Complete this self-test prior to beginning your laboratory experiment on rate and order.

1. State the characteristic units of the rate constant for a second-order reaction.

2. How can the order of a reaction be determined by a graphical procedure?

3. Do you have to determine the cell constant for your conductance cell in this experiment? Why?

4. Why should you keep the flasks containing alkaline solution stoppered?

5. Write the balanced equation for the reaction taking place in this experiment.

E. REFERENCES and SUPPLEMENTARY READINGS - These are references as well as suggestive readings for those students who may wish additional information.

1. Brennan, D., and C. F. H. Tipper, "A Laboratory Manual of Experiments in Physical Chemistry," McGraw-Hill, New York, 1967, pp. 176-181.

2. Crockford et al., "Laboratory Manual of Physical Chemistry," John Wiley, New York, 1975, pp. 212-218.

3. Daniels, F., and R. A. Alberty, "Physical Chemistry," John Wiley, New York, 1975, pp. 300-308.

4. Daniels et al., "Experimental Physical Chemistry," McGraw-Hill, New York, pp. 137-155.

5. Frost A. A., and R. G. Pearson, "Kinetics and Mechanism," John Wiley, New York, 1953, pp. 35-37.

6. Metz, C. R., "Theory and Problems of Physical Chemistry," McGraw-Hill, New York, 1976, pp. 183-222.

F. APPARATUS AND CHEMICALS

Conductivity cell, Wheatstone bridge and accessories; constant temperature bath at $25.0^\circ C \pm 0.1^\circ C$; two 300mL Erlenmeyer flasks; 1-hole rubber stopper; large pipette; 50mL pipette; 0.1 mL pipette; thermometer; stopwatch or timer; conductivity water; 0.0500 $\underline{N}$ NaOH; and pure methyl acetate.

G. PURPOSE

The purpose of this experiment is to investigate the kinetics of the alkaline hydrolysis (saponification) of an ester (methyl acetate) by sodium hydroxide, and to determine the specific rate constant for the reaction of sodium hydroxide with methyl acetate.

H. THEORY

INTRODUCTION

In this experiment you will determine the rate of a typical second-order reaction, the saponification of methyl acetate by sodium hydroxide. "Whenever a reaction occurs with a change in the number or kind of ions present so that the electrical conductivity changes, measurement of the resistance offers a convenient and accurate means of following the course of the reaction"(Frost & Pearson, 1953, p. 35). The reaction used in this experiment lends itself to study by conductometric methods.

The equivalent ionic conductances of acetate and hydroxide ions are quite different, and methanol and methyl acetate may be regarded as non-conducting. It is apparent, then, that the conductance of a solution consisting origi-nally of sodium hydroxide and methyl acetate in water will change as the saponification reaction proceeds. If the initial and final conductances of the solutions are known, the conductance at any intermediate time can be used to calculate the extent of reaction at that time.

PART I: Read the sections of your lecture textbook dealing with the following topics to obtain a basic understanding of the theory involved in this experiment:

Reaction rate, experimental methods for reaction rates, rate law, first-order and second order reactions.

Let a = the initial concentration of sodium hydroxide;
    b = the initial concentration of methyl acetate;
    L_o = the conductance of the system at zero time;
    L_f = the conductance at infinite time;
    L_t = the conductance at any time t;
C_1 & C_2 = arbitrary constants;
    x = concentration of sodium acetate at any time;
    k_2 = specific reaction rate constant (assuming a
              second reaction).

It can be shown that:

$$L_o = C_1 a$$
$$L_f = C_2 b + C_1 (a - b); \quad \text{where } a > b$$
$$L_t = C_1 (a - x) + C_2 x.$$

In terms of conductance relations we have

$$x = \frac{L_o - L_t}{C_1 - C_2}.$$

Also k_2, the reaction rate constant, may be shown to have
the value,

$$k_2 = \frac{1}{t(a-b)} \ln\left(\frac{b(a-x)}{a(b-x)}\right),$$

or for plotting purposes

$$k_2 t = \frac{1}{(a-b)} \ln\left(\frac{b(a-x)}{a(b-x)}\right) \quad (11\text{-}1)$$

which is the equation of a
straight line,

$$y = mx + b.$$

I. EXPERIMENTAL PROCEDURE (APPARATUS IS SAME AS IN EXP. 12)

1. Clean and dry a 300mL Ernlenmeyer flask. Check out a
special rubber stopper, through which has been drilled a
small hole to permit the introduction of a pipette. A
small cork is provided for sealing this hole.

2. Put the stopper in place in the flask, and, with the
small cork removed, pipette into the flask exactly 200 mL
of conductivity water. In a similar fashion add exactly
50 mL of 0.0500 $\underline{N}$ NaOH solution. Replace the small cork.

3. Clamp the flask in the constant temperature bath so
that the alkali solution is completely submerged. Agitate
the flask every minute or so in order to speed the
establishment of thermal equilibrium.

4. When the temperature of the alkali solution has reached that of the bath (allow 3 minutes plus 1 minute per degree difference between room and bath temperatures) rinse the conductance cell three times with small portions of the NaOH solution, fill the cell with the NaOH solution, and cork up the two arms of the cell.

NOTE: In order to avoid reaction of the alkali with carbon dioxide it is important that the Erlenmeyer flask and the cell containing the NaOH solution be stoppered except during the actual transfer of the solution.

5. Determine the resistance, R_o, of the cell filled with NaOH solution using the same technique as in Experiment 12. Since all subsequent calculations depend upon this determination, it is obvious that it should be made with great care.

6. Rinse the cell twice with conductivity water. While the next operations are being performed the cell should be allowed to stand filled with conductivity water.

7. Clean and dry another 300mL Erlenmeyer flask. Pipette 200 mL of the NaOH solution prepared in step 2 into this flask. Clamp the flask in the constant temperature bath as before, with the special stopper in place.

8. Remove the small cork and pipette 0.1 mL of pure methyl acetate into the flask. Record the time (to the nearest second) of addition. Remove the pipette and mix the solution vigorously for 2 to 3 seconds. Record the temperature of the methyl acetate.

9. Rinse the conductance cell three times with the reacting solution; take care to replace the small cork between additions. Finally, fill the cell with the solution from step 8, stopper the cell as before, and suspend the cell in the constant temperature bath.

10. Connect the cell to the Wheatstone bridge apparatus. When 5 minutes have elapsed since the combination of the reactants, begin making resistance measurements. For each measurement record the observed resistance measurements, and the time to nearest second at which the resistance was measured.

11. Make ten resistance determinations, R_t, at intervals of approximately 2 minutes.

J. CALCULATIONS

1. In this experiment a = 0.0100 $\underline{N}$. One may calculate b from the density of methyl acetate at the temperature recorded in step 8 of the PROCEDURE, and the volume of the NaOH solution to which the $0.1_{\circ}$mL of ester was added. The density of methyl acetate at $t^{\circ}C$ is given by the following empirical equation ($t = {}^{\circ}C$):

$$\rho = 0.9593 - 1.271 \times 10^{-3}t - 0.405 \times 10^{-6}t^2 - 6.09 \times 10^{-9}t^3.$$

L_o is the reciprocal of R_o which was measured in step 5. If b^o is not less than a, C_1/C_2 equals a constant value dependent only on a.

For a = .0100 $\underline{N}$, C_1/C_2 = 2.773. (C_2 may be found experimentally by making b $\geq$ a and determining the conductance at infinite time, since $L_f = C_2a$.

All necessary mathematical relationships have been given in PART II of the THEORY.

2. Plot $\frac{1}{(a-b)} \ln\frac{b(a-x)}{a(b-x)}$ versus $\underline{t}$ for each of your ten readings.

3. Your instructor may have you perform all possible calculations with a computer program. If so turn in your program and run $\underline{instead}$ of the DATA AND RESULT sheet at the end of this report. In any case, calculate k_2 (for a time unit of seconds and a concentration unit of moles per liter) for each of the ten determinations of the resistance of the reacting mixture. Calculate the average value of k_2 and append the average deviation from the mean.

4. What assumptions have been made in the derivation of the expression for x?

5. What is the half-life of the reaction?

K. EXAMPLES AND PROBLEMS

EXAMPLE 11-1: (Labowitz, L. C., and J. S. Arents, "Physical
Chemistry," Academic Press, 1969, p. 150.) This example
shows another method by which this experiment could have
been carried out, the titration method.

In an investigation of the kinetics of the alkaline
hydrolysis of ethyl acetate, Potts and Amis (J. Am. Chem.
Soc., 71, 2112(1949)) caried out the following experiment.
300 mL of water at 0°C was pipetted into a 600-mL flask and
100.00 mL of 0.0500 M ethyl acetate was added at the same
temperature. The flask was stoppered and allowed to reach
thermal equilibrium in a thermostat. The hydrolysis
reaction was then initiated by adding 100.00 mL of 0.1000 M
NaOH, also at 0°C, and shaking vigorously. If we assume
that the volumes of the starting solutions are strictly
additive on mixing, the resulting solution was initially
0.0100 M in ethyl acetate and 0.0200 M in NaOH. At various
intervals, t, 50.00-mL samples of the reaction mixture
were withdrawn, drained into a measured excess of 0.0200 M
HCl at 0°C (V_{HCl}), and titrated at 0°C with 0.0200 M NaOH,
(V_{NaOH}) mL being required. The concentration of NaOH in the
reaction mixture at equilibrium time (t = ∞) was determined
on samples permitted to stand at the reaction temperature
until no further change in the composition of the mixture
as a function of time could be detected. The results were
as follows:

t, min	V_{HCl}, mL	V_{NaOH}, mL
0	60.0	11.50
15	50.0	7.35
30	50.0	11.20
45	50.0	13.95
60	50.0	15.95
75	50.0	17.55
∞	50.0	24.00

Determine the order of this reaction and the rate constant, k.

$$k = \frac{2.303}{t(a-b)}\log\frac{b(a-x)}{a(b-x)}$$

$a = 0.0200 = [NaOH]_0$ $b = 0.0100 = [EtOAc]_0$

At t = 15 min

$[NaOH]$ = (50.0-7.35) x (0.0200 x 10^{-3}mole/0.0500 liter)

   = 0.01706 M = a - x

   x = a - 0.01706 = 0.0200 - 0.01706 = 0.00294

$[EtOAc]$ = b - x = 0.0100 - 0.00294 = 0.00706 M

$$k = \frac{2.303}{15(0.0100)} \log\left(\frac{0.0100(0.01706)}{0.0200(0.00706)}\right) = 1.260 \text{ liter /mole-min}$$

$k = 1.260, 1.136, 1.087, 1.053, 1.039,$

average $k = 1.097$ liter/mole-min

Thus, reaction is second order (as shown by the approximate constancy of k).

PROBLEM 11-1: What are the units of k for a second-order reaction? Show your work. (Assume t in seconds and Molar concentrations)

PROBLEM 11-2: (Metz, 1976, p. 199) The concentrations of bromine at various times after flash photolysis of a bromine-SF_6 mixture with $C_{Br_2}/C_{SF_6} = 3.2 \times 10^{-2}$

were reported by Degraff and Lang as:

$C_{Br} \times 10^5$,$\underline{M}$	2.58	1.51	1.04	0.80	0.67	0.56
t, μs	120	220	320	420	520	620

If these data are for the reaction

$$2Br \longrightarrow Br_2$$
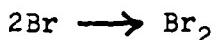
show that the reaction is pseudo-second-order and calculate k.

PROBLEM 11-3: (Metz, 1976, p. 213) The second-order reaction

$$CH^- + C_2H_5CH \longrightarrow C_2H_5C^- + H_2O$$

when studied in 0.1 $\underline{M}$ NaCH gave the pseudo-first order rate equation

$$-\frac{d}{dt}(C_{C_2H_5CH}) = kC_{C_2H_5CH}$$

with $k = 3 \times 10^5$ s^{-1}. Find the rate constant for the second-order reaction.

ANS: $k_2 = k/C_{CH^-} = 3 \times 10^6$ $M^{-1}s^{-1}$

L.   DATA AND RESULTS   (DO NOT COMPLETE IF YOU DO A COMPUTER
     PROGRAM)

1. R_o _____

2. L_o _____

3. L_f _____

4.   a _____

5.   Temperature of methyl acetate   _____

6.   Density of methyl acetate   _____

7.   b   _____

8.   Time of addition   _____

I	II	III	IV	V	VI	VII
R_t	L_t	x	a-x	b-x	t	k_2

$k_2 =$ _____ $\pm$ _____ at _____ $^{o}C.$

APPENDIX K

CONDUCTANCE OF STRONG AND WEAK ELECTROLYTES

APPENDIX K

EXPERIMENT 12:   CONDUCTANCE OF STRONG AND WEAK ELECTROLYTES

A.   STUDY GUIDE AND REVIEW ASSIGNMENT

1.   Read the sections of your lecture textbook dealing with
Conductance (Irreversible processes in solution).   This will
give you a short overview of the material which is
contained in this experiment.

2.   Work the following problem to prepare you for the types
of calculations you will be expected to make in this
experiment:

   a.   (Daniels, 1975, p. 381)   A conductance cell was
calibrated by filling it with a 0.02 M solution of potassium
chloride (conductivity = 0.2768 $ohm^{-1}m^{-1}$) and measuring
the resistance at $25°C$, which was found to be 457.3 ohms.
The cell was then filled with a calcium chloride solution
containing 0.555 gram of $CaCl_2$ per liter.   The measured
resistance was 1050 ohms.   Calculate (a) the cell constant
for the cell, (b) the conductivity of the $CaCl_2$ solution,
and (c) the molar conductivity of $CaCl_2$ at this concentration.
ANS: (a) 126.6 m^{-1}, (b) 0.126 $ohm^{-1}m^{-1}$, and (c) $\dfrac{0.0241 \ m^2}{ohm^{-1}mol^{-2}}$.

3.   Read the THEORY and PROCEDURE sections of this
experiment prior to coming to lab.

4.   Complete the PRELIMINARY REPORT prior to lab.

5.   Supply the definitions for the KEY WORDS.   The majority
of these terms are discussed in the THEROY section and in
your lecture textbook.

6.   Your instructor will give you your conductance cell.
You should use this same cell in any other conductance
work   required   in this course.

B.   OBJECTIVES - You shall be able to:

1.   Define and/or briefly discuss the KEY WORDS.   This
should aid your learning about conductance.

2.   Determine the conductance of strong and weak electrolytes.

3.   Calculate equivalent conductance from specific
conductances or from dissociation constant (See EXAMPLES
AND PROBLEMS).

4. Calculate the dissociation constant from the degree of dissociation for any given electrolyte.

C. KEY WORDS: (Supply equations where possible.)

Cell constant, K

Conductance, L

Conductivity, 1/r

Degree of dissociation, α

Electrolytes, strong and weak

Equivalent conductance, Λ

Infinite dilution

Kohlrausch's Law

Polarization

Resistivity, or specific resistance, r

Specific conductance, L_s

Wheatstone bridge

D. PRELIMINARY REPORT - Answer the following questions prior to coming to the laboratory. You may be required to turn this sheet in for grading or you may have a quiz prior to performing the experiment.

1. Derive Equation 12-6 from Equations 12-4 and 12-5.

2. Discuss why you should plot Λ versus $c^{\frac{1}{2}}$ rather than c.

3. What is the objective of plotting Λ versus $c^{\frac{1}{2}}$? (What is determined?)

4. Why is the cell constant determined? Why can't you simply determine the conductance of a solution directly?

5. Why is A.C. rather than D.C. used in this experiment?

6. Draw a Wheatstone bridge circuit and show how to solve for the resistance of the conductance cell.

E.   REFERENCES and SUPPLEMENTARY READING - These are
references as well as suggestive readings for those students
who may wish additional information.

1.   Daniels, F., and R. A. Alberty, "Physical Chemistry,"
John Wiley, New York, 1975, pp. 365-370.

2.   Daniels, et al., "Experimental Physical Chemistry,"
McGraw-Hill, New York, 1970, pp. 167-177.

3.   Kemp, M. K., "Physical Chemistry for Engineering and the
Physical Science," Marcel Dekker, 1974, pp. 10.74-10.83.

4.   Metz, C. R., "Theory and Problems of Physical Chemistry,"
McGraw-Hill, New York, 1976, pp. 132-135.

5.   Salzberg, et al., "Physical Chemistry," Academic Press,
New York, 1969, pp. 201-205.

F.   APPARATUS AND CHEMICALS

Conductance apparatus: oscillator, slide wire resistance,
standard resistance box, earphones, conductance cell;
thermostat bath at $25.0^\circ \pm 0.1^\circ C$; six 100mL glass stoppered
flasks; 50 mL pipette; connecting wire and connectors;
labels.   0.0300 $\underline{N}$ KCl solution; water of very high purity;
weak electrolyte unknowns for which resistance must be
determined.

An oscilloscope can be used instead of earphones as a null
point indicator. Check with your instructor if you desire
to use this option.

G.   PURPOSE - The main purposes of this experiment is to:

1.   Familarize the student with techniques for the
determination of the conductance of electrolytic solutions.

2.   Illustrate the behavior of strong and weak electrolytes.

H.   THEORY

          If a solution of an electrolyte is introduced
between two electrodes of area A, which are a distance ℓ
apart, then the total conductance is the reciprocal of the
total resistance R, i.e., $L = 1/R$. But the resistance of
a conductor is given by $R = r\ell/A$, where r is the specific
resistance. Substituting, we obtain

$$L = \frac{1}{R} = \frac{A}{r\ell} = \frac{AL_s}{\ell} \text{ ohm}^{-1} \qquad (12\text{-}1)$$

where L_s, the <u>specific conductance</u> is defined as the reciprocal of the specific resistance. L_s is the conductance of a one-centimeter cube of material and has the units of reciprocal ohms, or mhos per centimeter.

The specific conductance could in theory be determined by measuring the resistance of a cell in which a one centimeter cube of solution is enclosed between two platinized platinum electrodes exactly one centimeter on edge and exactly one centimeter apart. Experimentally this is difficult, and in practice a vessel containing two electrodes of any convenient size and distance apart is used together with a solution whose specific conductance has been accurately determined. This is a <u>conductance cell</u>, and the effective ratio ℓ/A is called the <u>cell constant</u> K.

The cell constant is determined experimentally by filling the conductance cell with a solution for which L_s is known and measuring the resistance, R, of the cell, giving:

$$L_s = \frac{K}{R} \text{ ohm}^{-1}\text{cm}^{-1} \qquad (12\text{-}2)$$

or $K = L_s R$. Once K is known for a particular cell, the cell can then be used to determine L_s for unknown solutions.

The <u>equivalent conductance</u> of a solution, Λ, is defined as the product of the specific conductance and the volume, V, in cc, of that amount of solution which contains one equivalent of electrolyte. But V = 1000/C, where C is the normality, giving

$$\Lambda = VL_s = \frac{1000 \, L_s}{C} \text{ ohm}^{-1}\text{cm}^2\text{equiv}^{-1} \qquad (12\text{-}3)$$

It has been found that Λ increases with decreasing concentration, even though Λ, by definition, is the conductance of a constant amount of electrolyte – namely, one equivalent. Arrhenius explained this by the assumption that dissociation of electrolyte increases as the concentration decreases. Assuming that the mobility of the ions was constant with changing concentration and that an electrolyte was completely dissociated at <u>infinite dilution</u>, Arrhenius proposed

$$\alpha = \frac{\Lambda}{\Lambda_0} \qquad (12\text{-}4)$$

where α is the <u>degree of dissociation</u> of the electrolyte, Λ its equivalent conductance, and Λ_0 its equivalent conductance at infinite dilution. Substituting this expression into the apparent dissociation constant of a binary electrolyte,

$$K_D = \frac{\alpha^2 C}{1 - \alpha} \tag{12-5}$$

which can be rearranged to give: (See Preliminary Report 1)

$$\frac{1}{\Lambda} = \frac{\Lambda C}{\Lambda_o^2 K_D} + \frac{1}{\Lambda_o}. \tag{12-6}$$

This equation may be tested by a plot of $1/\Lambda$ against ΛC. If the theory is correct this plot should be a straight line with slope $1/\Lambda_o^2 K_D$ and with intercept on the $1/\Lambda$ axis equal to $1/\Lambda_o$. The experimental results for some electrolytes conform rather closely to the Arrhenius theory. Such electrolytes are known as weak electrolytes because, except in extremely dilute solutions, their degree of dissociation is very small.

Other electrolytes, known as strong electrolytes, exhibit a relatively high apparent degree of dissociation, even in concentrated solutions. Conductance data for dilute solutions of strong electrolytes conform to the following empirical equation, proposed by Kohlrausch:

$$\Lambda = \Lambda_o - A\sqrt{C} \qquad \text{where C is the normality} \tag{12-7}$$

and A is a constant which depends upon the type of electrolyte.

For Equation 12-7 we plot Λ versus $\sqrt{C}$ rather than Λ vs C, since the slope of the plot increases rapidly as zero concentration is approached, making it difficult to extrapolate to Λ_o. However, the curve is linear at low concentrations, slope of A, and the intercept of the extrapolation to zero concentration is Λ_o.

For a weak electrolyte Kohlrausch's Law may be used to determine Λ_o. According to this law at infinite dilution the ions behave independently of each other so that $\Lambda_o = \lambda_o^+ + \lambda_o^-$ in which λ_o^+ is equal to the equivalent conductance of the cation at infinite dilution and λ_o^- is equal to the equivalent conductance of the anion at infinite dilution. Since the above equation is valid for all electrolytes, it can be shown for acetic acid, HAc, that at infinite dilution: (See EXAMPLE 12-5)

$$\Lambda_o(\text{HAc}) = \Lambda_o(\text{HCl}) + \Lambda_o(\text{NaAc}) - \Lambda_o(\text{NaCl}) \tag{12-8}$$

That is Λ_o may be obtained algebraically from Λ_o values for three strong electrolytes where (HAc) itself is a weak electrolyte.

The measurement of specific conductance and the equivalent conductance of solutions is based on the measurement
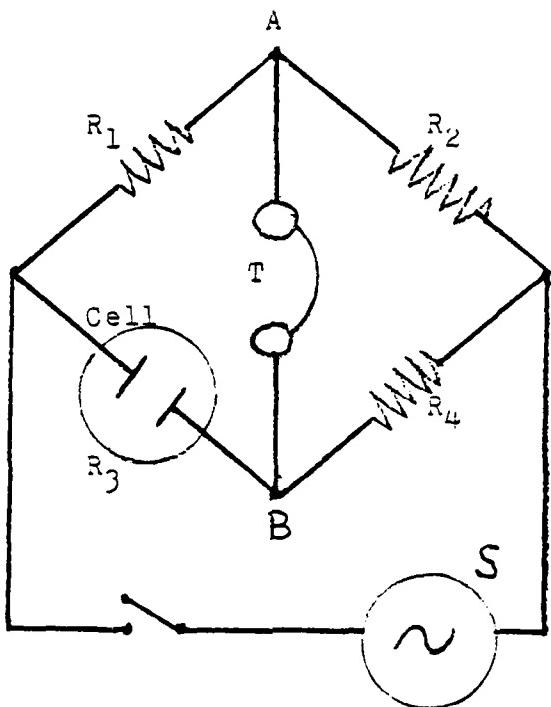
FIGURE 12-1.

Wheatstone Bridge Circuit

of resistance. This is usually accomplished by means of a
Wheatstone bridge. Alternating current of about a thousand
cycles per second is used to prevent complications at the
electrodes. Direct current would produce gas bubbles, i.e.,
electrolytic decomposition, which would greatly affect the
resistance of the cell and polarize the electrodes. The
electrodes are platinized to further minimize the evolution
of gases at the electrodes.

The Wheatstone bridge circuit is shown in FIGURE 12-1.
R_1, R_2, and R_4 are known resistances, R_3 represents the re-
sistance of the conductance cell, S is a source of alternat-
ing current, and T is earphones or some other device used to
detect the balance of the bridge circuit. When points A and
B are at the same potential no current will pass through the
headset. Therefore no sound will be heard and the bridge is
assumed to be balanced. Thus R_3 can be calculated from

$$R_3 = \frac{R_1 R_4}{R_2}.$$

(12-9)

I. EXPERIMENTAL PROCEDURE

The resistance of the conductance cell is determined by means of a Wheatstone bridge. Alternating current must be used to avoid polarization about the electrodes. In the adaptation of the Wheatstone bridge circuit to AC several additions are made to the simple DC circuit.

A set of earphones, or a cathode ray tube is used as a null point indicator. Refer to the separate instructions and diagram for the bridge.

PART I. Resistance Determination - General Directions

1. Fill the cell with the solution whose resistance is to be determined; place the cell in the thermostat bath, which is regulated to 25°C.

2. Connect the cell to the bridge. After thermal equilibrium has been established, carry out the steps as indicated in the bridge instructions.

PART II. Resistance of Conductivity Water

In this experiment our interest is focused on the conductance due to ions produced by dissociation of strong and weak electrolytes. Conductance effects due to the solvent, therefore, must be eliminated or accounted for. It is customary to reduce the solvent conductance through the use of water of very high purity where the actual specific conductance of this very pure conductivity water is determined by direct measurement.

The conductivity cell was filled with water when stored, to prevent the electrodes from drying out; since the electrodes are ruined if they become dry, the cell should never be left unfilled for more than a few minutes. Since the resistance of the cell filled with conductivity water is too large to be measured directly with the available resistances, it must be determined indirectly; the method employed is based upon Ohm's Law for resistances in parallel. (SEE EXAMPLES)

(If necessary use the method described in your Electrochemistry Experiments to replate the electrodes.)

1. Check the connections in the bridge. Introduce in place of the conductance cell an external resistance box that can be set at resistances of between 5,000 and 10,000 ohms.

2. Working in pairs determine accurately the value of several external resistances by having one person adjust the resistance box to a resistance that is unknown to the other person and then let the second person balance the bridge until the correct resistance is found. This process will provide practice for operating the equipment and obtaining

correct values for the resistance. After the one person has developed this skill, they should trade places and allow the other one to determine the unknown resistances.

3. Rinse the cell three times with small portions of conductivity water; then fill it. Connect the cell in parallel with the external resistance and determine the total resistance. Follow complete procedure in PART I. Record the number of the cell and the resistances determined.

4. Adjust the external resistance to a value slight different from that established in II-1 and repeat II-2 and II-3.

PART III. Conductance of Strong Electrolytes

1. Using the same cell continue the procedure for strong electrolytes.

2. Clean and dry six glass-stoppered flasks. Into one pour approximately 100 mL of 0.0300 $\underline{N}$ KCl solution. Into each of the others pipette 50 mL of conductivity water.

3. Rinse the pipette with small portions of 0.0300 $\underline{N}$ KCl. DO NOT USE THE SOLUTION IN THE FIRST FLASK FOR THIS PURPOSE. Pipette 50 mL of 0.0300 $\underline{N}$ KCl from the first flask into the second flask. Mix the contents of the second flask throughly.

4. Employing the technique which will be demonstrated by the instructor, rinse the pipette with the solution in the second flask and pipette 50 mL of this solution into the third flask; mix the contents of the third flask thoroughly.

5. In the manner outlined above continue the two-fold dilutions until six solutions, one each of the following normalities, are prepared: 0.03000, 0.01500, 0.00750, 0.00375, 0.001875, and 0.000938. Label each flask clearly.
The cell constant, K, for any cell is best determined by measurement of the resistance of the cell when it is filled with a standard solution of KCl whose specific conductance is known. The dilutions called for above must be carried out with great care, especially since the 0.00750 $\underline{N}$ solution which results from the second dilution will be employed as a standard for cell constant determination.

6. Starting with the most dilute solution, determine and record the resistance of the cell when it is filled with each of the six KCl solutions. Be sure to rinse the cell several times with small portions of the solution under test before filling the cell. The complete procedure in PART I must be followed in each case.

PART IV. Conductance of Weak Electrolytes

In this part of the experiment you will determine the specific
conductances of a number of solutions of a weak electrolyte.
Each pair of students will carry out determinations on a
different electrolyte; the concentration of the master solu-
tion will be given you by the instructor.

1. Prepare six solutions of weak electrolyte of different
concentrations. Follow the procedure outlined in III-2 through
5.

2. Starting with the most dilute solution, determine and re-
cord the resistance of the conductance cell when it is filled
with each of the six weak electrolyte solutions. Be sure to
rinse the cell several times with small portions of the solu-
tion under test before filling the cell. The complete proce-
dure in PART 1 must be followed in each case.

3. Record the temperature of the thermostat bath.

J. CALCULATIONS

1. Compute the value of the cell constant K from the Equa-
tion 12-2, $K = L_S R$, the observed resistance of the 0.00750 $\underline{N}$
KCl solution, and the known specific conductance of KCl at
this concentration, 0.001074 $ohm^{-1}cm^{-1}$ at 25°C.

2. Calculate the specific conductance of each of the KCl
solutions and of the conductivity water; correct the solution
values for water conductance. Using the corrected specific
conductances, calculate the equivalent conductance at each
concentration.

3. Repeat the calculations in 2 for the weak electrolyte
solutions.

4. For each system prepare a plot of $1/\Lambda$ against Λc.

5. For each system prepare a plot of Λ against $c^{1/2}$.

6. For each system determine Λo by extrapolation of the
appropriate linear plot to zero concentration (infinite dilu-
tion). Note that in the case of the weak electrolyte this is
not an accurate method for determination of Λo.
    You may use a computer program for a least squares fit to
obtain the slope and intercept for the KCl data.

7. Use equations (4) and (5) to calculate the value of K_D
for KCl solutions at each concentration investigated. Are
the resulting values of K_D constant? Explain briefly.

K. EXAMPLES AND PROBLEMS

EXAMPLE 12-1: For two resistors of 10000 ohms and X ohms in parallel, find the   value   of X if the total resistance of the two resistors is 9000 ohms.

From Ohm's Law for resistance in parallel

$$\frac{1}{R_T} = \frac{1}{R_1} + \frac{1}{R_2}$$

$$\text{or} \quad R_T = \frac{R_1 R_2}{R_1 + R_2}$$

Therefore, letting $X = R_2$, we obtain $X = R_2 = 90{,}000$ ohms.

EXAMPLE 12-3: For the Wheatstone bridge circuit shown in Figure 12-1, prove that

$$\frac{R_1}{R_2} = \frac{R_3}{R_4} \qquad \text{where } R_3 = R_{cell}$$

$$E_1 = I_1 R_1; \quad E_2 = I_2 R_2; \quad E_3 = I_3 R_3; \quad E_4 = I_4 R_4$$

$$I_1 R_1 = I_3 R_3; \quad I_2 R_2 = I_4 R_4$$

$$\frac{I_1 R_1}{I_2 R_2} = \frac{I_3 R_3}{I_4 R_4}$$

When the bridge is balanced

$$I_1 = I_2; \quad I_3 = I_4 \qquad \text{and therefore,}$$

$$\frac{R_1}{R_2} = \frac{R_3}{R_4}.$$

EXAMPLE 12-3:   (Metz, 1976, p. 141) A conductivity cell was calibrated using 0.010 $\underline{N}$ KCl ($L_s = 0.0014087$ ohm^{-1}cm^{-1}) in the cell and the measured resistance was 688 ohms. Find the cell constant.

From Equation 12-2, $K = L_s R$

$K = (0.0014087 \text{ ohm}^{-1}\text{cm}^{-1})(688 \text{ ohm}) = 0.97 \text{ cm}^{-1}.$

EXAMPLE 12-4:   (Metz, 1976, p. 141) For the cell in EXAMPLE 12-3, a 0.0100 $\underline{N}$ AgNO$_3$ solution in the same cell had a resistance of 777 ohms. What is the equivalent conductance?

$$L_s = \frac{k}{R} = 0.97 \text{ cm}^{-1}/777 \text{ ohm} = 0.001248 \text{ ohm}^{-1}\text{cm}^{-1}$$

Using Equation 12-3

$$\Lambda = \frac{1000 \, L_s}{C} = \frac{1000 \times 0.001248 \text{ ohm}^{-1}\text{cm}^{-1}}{0.0100 \text{ equiv}/(\text{cm} \times \text{cm} \times \text{cm})}$$

$$\Lambda = 124.8 \text{ ohm}^{-1}\text{cm}^2\text{equiv}^{-1}.$$

EXAMPLE 12-5: (Adamson, W. A., <u>Understanding Physical Chemistry</u>, 1964, p. 264) Given the following equivalent conductivities at 25°C: HCl, 426; NaCl, 126; NaC (Sodium Crotonate), 83; calculate the dissociation constant of (H^+C^-), crotonic acid. Also given is that the specific conductivity of a 0.00100 $\underline{M}$ solution of the acid is 3.83×10^{-5} ohm^{-1}cm^{-1}. Neglect variation of equivalent conductivities with concentration.
■----------
Using Kohlrausch's Law, Equation 12-8

$$\Lambda^{\circ}_{H^+C^-} = \Lambda^{\circ}_{HCl} + \Lambda^{\circ}_{NaC} - \Lambda^{\circ}_{NaCl}$$

$$= 426 + 83 - 126 = 383.$$

Thus the actual ion concentrations in the 0.00100 $\underline{M}$ solution of the acid is then:

$$C = 1000 \, L_s/\Lambda^{\circ} = \frac{1000 \times 3.83 \times 10^{-5}}{383} = 10^{-4}\underline{M} = .00010 \underline{M}$$

The concentration of the undissociated acid is then

$$.00100 - .00010 = .00090 = 9.0 \times 10^{-4}\underline{M}$$

For $\quad HC = H^+ + C^-$

$$K_d = (H^+)^2/(HCl) = \frac{(10^{-4})^2}{9 \times 10^{-4}} = \underline{1.11 \times 10^{-5}}.$$

PROBLEM 12-1: (Kemp, 1974, p. 10-88) Calculate the cell constant of a cell which gives a conductance reading of 0.120 ohm^{-1} for 0.010 $\underline{M}$ KCl at 25°C, and $\Lambda = \dfrac{141.27 \text{ cm}^2}{\text{ohm}^{-1}\text{equiv.}^{-1}}$.

ANS: 0.01177 cm^{-1}

PROBLEM 12-2: (Kemp, 1974 p. 10-88) What conductance would be measured with the cell in PROBLEM 12-1 for a 0.0050 N solution of NH_4Cl at $25^{\circ}C$ if $\Lambda = 143.5$ $ohm^{-1}cm^2equiv^{-1}$?

ANS: 0.06096 ohm^{-1}

PROBLEM 12-3: Outline the steps involved in going from the expression $L = AL_s/\ell$ to the expression $\Lambda = 1000 \ L_s/C$, where symbols are defined as in THEORY section.

PROBLEM 12-4: The equivalent conductance of silver chlorate at a series of concentration C (equiv/liter) are reported below (Jones, J. Am. Chem. Soc., 69, 2066, 1957).

C	Λ
.0010256	123.43
.0013694	122.94
.0029782	121.14
.0032500	120.95

Find Λ_o for this compound. (Hint Plot Λ vs. $C^{\frac{1}{2}}$.)

ANS: 126.62

L. DATA AND RESULTS

RESISTANCE

1. Conductivity Water (ohms) _____

2. KCl – 0.00750 N (ohms) _____

3. Cell constant (cm^{-1}) _____

4. L_s – Conductivity Water ($ohm^{-1}cm^{-1}$) _____

5.

N-KCl	RESISTANCE	L_s	Λ	Corrected Λ
.03000	_____	_____	_____	_____
.01500	_____	_____	_____	_____
.00750	_____	_____	_____	_____
.00375	_____	_____	_____	_____
.001875	_____	_____	_____	_____
.000938	_____	_____	_____	_____

6. N-Weak Electrolyte-Name-_____

_____	_____	_____	_____	_____
_____	_____	_____	_____	_____
_____	_____	_____	_____	_____
_____	_____	_____	_____	_____
_____	_____	_____	_____	_____
_____	_____	_____	_____	_____

7. Λ_o – KCL _____ (from graph)

8. Λ_o – Weak Electrolyte _____ (from graph)

9. Λ_o – Accepted value from instructor or Handbook _____

10.

N-KCL	K_D	N-Weak Electrolyte	K_D
.03000	_____	_____	_____
.01500	_____	_____	_____
.00750	_____	_____	_____
.001875	_____	_____	_____
.000938	_____	_____	_____

APPENDIX L

REFRACTIVE INDEX

APPENDIX L

EXPERIMENT 13: REFRACTIVE INDEX

A. STUDY GUIDE AND REVIEW ASSIGNMENT

1. Read the appropriate sections of your lecture textbook
to obtain an overview of refractive index. Do this prior
to coming to lab.

2. Read the THEORY and PROCEDURE sections of this
experiment prior to coming to lab.

3. Supply definitions for the KEY WORDS. The majority of
these are discussed in your lecture textbook.

4. Complete the PRELIMINARY REPORT of this experiment
prior to lab.

5. You should read the procedure section of the
Refractometer guide prior to coming to class.

6. Be prepared to discuss how the refraction of atoms (H)
and groups of atoms (CH_2) can be determined from the molar
refraction of compounds.

B. OBJECTIVES - You shall be able to:

1. Define and/or briefly discuss the KEY WORDS on this
page.

2. Calculate the Molar Refractions of various parts of a
molecule.

3. Learn how to use a Refractometer.

C. KEY WORDS: (Supply equations where possible.)

Additive property

Constitutive property

Dielectric constant

Molar refraction, R

Refractometer

Snell's law

D. PRELIMINARY REPORT - Complete this self-test prior to beginning your laboratory experiment on refractive index.

1. Briefly explain the operation of a refractometer.

2. What is the difference between an additive property and a constitutive property?

3. Why does the refractive index vary with temperature?

4. What is one application of Molar Refraction?

E. REFERENCES and SUPPLEMENTARY READINGS - These are references as well as suggestive readings for those students who may wish additional information.

1. Daniels et al., "Experimental Physical Chemistry," McGraw-Hill, New York, 1970, pp. 456-458.

2. Kittsley, Scott L.,"Physical Chemistry," Barnes & Noble, New York, 1969, pp. 36-37.

3. Labowitz, L. C., and J. S. Arents, "Physical Chemistry," Academic Press, New York, 1969, p. 56.

4. Shoemaker, D. P., and C. W. Garland, "Experiments in Physical Chemistry," McGraw-Hill, New York, 1962, pp. 425-429.

F. APPARATUS AND CHEMICALS

Refractometer, thermostated at $20^{\circ}C$; sodium-vapor lamp (optional); eye droppers; clean cotton-wool; acetone wash bottles; reagent-grade acetone, methanol, methyl acetate, ethyl acetate, ethylene chloride, n-heptane, carbon tetrachloride, chloroform, toluene, benzene, bromobutane; acetone or methanol for rinsing; and large bottle for disposal of waste solutions.

G. THEORY

The refractive index, n, is a measure of the bending of light rays at the interface of two substances when the light passes from one substance to the other. It is dependent upon the optical densities of the substances and upon the velocity of light. Usually one of the substances is air, whose optical density is considered to be a constant. The light source used is usually the D-line of sodium. Then the refractive index is dependent only upon the optical density of the substance. The optical density is dependent upon the molecular arrangement, the atoms present in the molecule, and the density of the materials. Since the density varies with temperature so also does the refractive index. It can be shown that the quantity, molar refraction, R, is defined as follows:

$$R = \frac{M(n^2 - 1)}{\rho(n^2 + 2)}$$

where n is the refractive index, M the molecular weight, and ρ the density. The value of the molar refraction is made up of the sum of the contributions from the various atoms and their arrangements in the molecule. These contributions are nearly independent of each other.

Molar refraction is also defined as the product of the specific refraction, r, and the molecular weight:

$$R = Mr,$$

where

$$r = \frac{(n^2 - 1)}{\rho(n^2 + 2)}.$$

The relation does not always give a constant value of r as the density is varied, and hence must be considered as an approximation. There are other empirical relationships, such as, that of Eykiman which apply to many liquids over a considerable range of temperatures, however, they will not be considered here.

We may state the Law of Refraction in two parts. First, when a ray of light passes from a less dense medium into a more dense medium, the ray is bent towards the normal (to the surface of the medium). Conversely, when the ray passes from a more dense medium, it is bent away from the normal. It should be noted that the incident ray, the normal, and the refracted ray all lie in the same plane. Thus, for any given wavelength, the ratio of the sine of the angle of incidence to that of the angle of refraction is the refractive index, n. This is known as Snell's Law.

The molar refraction depends upon the number (additive property) and the kinds (constitutive property) of atoms and bonds present. In this experiment, the proposal

that molar refractions of various parts of a molecule when added approximates the molar refraction of the substance is considered. Also, the refractive index is used to determine the concentration of a solution.

H. PROCEDURE

1. Read the section of the refractometer manual dealing with the procedure and cleaning of the prisms.

2. Connect the refractometer to a circulating constant temperature bath and adjust to $20^{\circ}C$.

3. Clean the prisms carefully with methanol (or absolute acetone). Determine the refractive index of distilled water. Allow a minute or two for the water sample to come to $20^{\circ}C$. Using the manual determine the correction to be applied to your readings. Three or more independent readings should be made for each water sample, however, a new portion need not be used for each of the readings.

4. Read the refractive indices of the following compounds: methyl acetate, ethyl acetate, ethylene chloride, n-heptane, carbon tetrachloride, chloroform, methanol, toluene, benzene, bromobutane, and acetone. Clean the prisms thoroughly between samples.

5. Clean two burettes. Use these to make up solutions of methanol and chloroform. Plastic or aluminum foil covered vials may be used for storage containers. Loss due to evaporation should be avoided. The following ratios are suggested:

	Methanol (mL)	Chloroform (mL)
(1)	2	8
(2)	4	6
(3)	6	4
(4)	8	2

6. Record the refractive indices of the above solutions.

7. Record the refractive index of the unknown mixture of methanol and chloroform provided by the instructor.

8. From the literature obtain the densities of the various pure compounds.

I. CALCULATIONS

From your values of n, calculate the specific refractions and the molar refractions of the compounds.

From the molar refractions of methyl acetate and ethyl acetate, calculate the refraction of CH_2 (additive property). From this value and the molar refraction of ethylene chloride, calculate the refraction of Cl (atomic property). From this value and the molar refraction of chloroform, calculate the refraction of H. From the data on n-heptane, calculate the refraction of H. Calculate the refraction of CH_2 from the data on benzene and toluene.

Plot the refractive index of the mixture as ordinate against the mole fraction as abscissa. (Don't forget the points for the pure compounds.) From this graph, determine the concentration of the unknown in mole fraction.

J. EXAMPLES AND PROBLEMS

EXAMPLE 13-1: (Kittsley, 1969, p. 37) For ethyl acetate at $20°C$, n = 1.37, ρ = 0.901, M = 88.1. Calculate R using (1) the definitional equation, and (2) using the data below.

Atomic and Constitutive Refractions

C	2.42	Double bond in C=C	1.73
H	1.10	Triple bond in C≡C	2.40
Cl	5.97	Carbonyl oxygen	2.21
Br	8.87	Hydroxyl oxygen	1.53
I	13.90	Ether oxygen	1.64

Esters contain one carbonyl oxygen and one ether oxygen.

Molar Refraction can be determined by adding the appropriate atomic and constitutive refractions. For example, the refraction associated with a CH_2 group is equal to:

(R of $n\text{-}C_7H_{16}$) - (R of $n\text{-}C_6H_{14}$).

The atomic refraction of a hydrogen atom is equal to:

$$\frac{(R \text{ of } n\text{-}C_6H_{14}) - 6(R \text{ of } CH_2)}{2}.$$

The atomic refraction of carbon is (R of CH_2) - 2(R of H). Therefore, for the above example;

(1) $\quad R = \dfrac{M}{\rho} \dfrac{n^2-1}{n^2+2} = \dfrac{(88.1)((1.37)^2-1)}{(0.901)((1.37)^2+2)} = \dfrac{(88.1)(1.88-1)}{(.901)(1.88+2)} = 22.2.$

(2) From the data in the table above:

1 carbonyl oxygen	2.21
1 ether oxygen	1.64
4 C's (4 x 2.42)	9.68
8 H's (8 x 1.10)	8.80
R =	22.33

EXAMPLE 13-3: Given the following molar refractions:
CH_3I = 19.5, CH_3Br = 14.5, HBr = 9.9, and CH_4 = 6.8.
Calculate the value for CH_2BrI.

Molar refractions are treated as additive, and there are
several ways of combining the data to get the desired answer;
here is one way.

$$R\ (CH_2) = R\ (CH_3Br) - R\ (HBr) = 14.5 - 9.9 = 4.6$$
$$R\ (H) = \frac{R\ (CH_4) - R\ (CH_2)}{2} = \frac{(6.8 - 4.6)}{2} = 1.1$$
$$R\ (I) = R\ (CH_3I) - R(CH_2) - R\ (H) = 13.8$$
$$R\ (CH_2BrI) = R\ (CH_3Br) - R\ (H) + R\ (I) = 27.2$$

PROBLEM 13-1: (Kittsley, 1969, p. 40) Calculate the molar
refraction of acetone using the data in EXAMPLE 13-1. The
experimental value using the definitional equation is
equal to 16.2.

PROBLEM 13-2: (Kittsley, 1969, p. 40) The molar refraction
of a certain compound is equal to 26.51. The density is
equal to 1.595 g/cm^3. The molecular weight is 153.84.
Calculate the refractive index to four significant figures.

PROBLEM 13-3: Given the following molar refractions:
$CH_3CH_2CH_2CH_3$ = 20.6, CH_3CH_2CH = 12.9, and CH_3CH = 8.3.
Calculate R for $CH_3CH_2CH_2CH_2CH$.

K.   DATA AND RESULTS

Sample	n	Density (g/cm^3)
1.		
2.		
3.		
4.		
5.		
6.		
7.		
8.		
9.		
10.		
11.		
12.		

Mixture No.	mL of Methanol	mL of Chloroform	n
13.			
14.			
15.			
16.			

	Sample	Specific Refraction (r)	Molar Refraction R
17.	_____	_____	_____
18.	_____	_____	_____
19.	_____	_____	_____
20.	_____	_____	_____
21.	_____	_____	_____
22.	_____	_____	_____
23.	_____	_____	_____
24.	_____	_____	_____
25.	_____	_____	_____
26.	_____	_____	_____
27.	_____	_____	_____
28.	_____	_____	_____

29. Refraction of CH_2 _____

30. Refraction of Cl _____

31. Refraction of H _____

32. Refraction of H from n-heptane_____

33. Refraction of CH_2 from benzene_____

	Mixture No.	Mole Fraction of Chloroform
34.	_____	_____
35.	_____	_____
36.	_____	_____
37.	_____	_____

38. Concentration of unknown (mole fraction of
chloroform) _____

APPENDIX M

ATOMIC EMISSION SPECTRA

APPENDIX M

EXPERIMENT 14: ATOMIC EMISSION SPECTRA

A. STUDY GUIDE AND REVIEW ASSIGNMENT

1. Read the appropriate sections of your lecture textbook to obtain an overview of atomic emission spectra. Do this prior to coming to lab.

2. Read the THEORY and PROCEDURE sections of this experiment prior to coming to lab.

3. Supply definitions for the KEY WORDS. The majority of these terms are discussed in your lecture textbook.

4. Complete the PRELIMINARY REPORT of this experiment prior to lab.

5. Be prepared to discuss the Rydberg equation.

B. OBJECTIVES - You shall be able to:

1. Define and/or briefly discuss the KEY WORDS below.

2. Determine the frequency of observed spectral lines when compared to lines of known frequency.

3. Use the Rydberg equation and your determined frequencies to calculate a value for the Rydberg equation.

4. Learn how to use a spectroscope.

5. Study and calibrate a rudimentary visible-region spectroscope.

6. Observe some emission lines in the de-excitation spectra of helium, mercury, sodium, and hydrogen.

C. KEY WORDS

Balmer series

Emission

Rydberg constant

Rydberg equation

Spectroscope

D.   PRELIMINARY REPORT - Complete this self-test prior to beginning your laboratory experiment on atomic emission spectra.

1.   Briefly explain the operation of a gas-discharge tube.

2.   Briefly discuss how line spectra are formed.

3.   What is the longest period of time that you may hold down the operation key?

4.   Calculate λ, ν, ν_0 and $\bar{\nu}$ for a beam of blue light with a wavelength of 4500 Å.

E.   REFERENCES and SUPPLEMENTARY READINGS - These are references as well as suggestive readings for those students who may wish additional information.

1.   Crockford et al., "Laboratory Manual of Physical Chemistry," John Wiley, New York, 1975, pp. 303-306.

2.   Daniels, F., and R. A. Alberty, "Physical Chemistry," John Wiley, New York, 1975, pp. 392-395.

3.   Daniels et al., "Experimental Physical Chemistry," McGraw-Hill, New York, 1970, pp. 242-245.

4.   Kemp, M. K., "Physical Chemistry for Engineering and the Physical Science," Marcel Dekker, 1974, pp. 6.10-6.17.

5.   Metz, C. R., "Theory and Problems of Physical Chemistry," McGraw-Hill, New York, 1976, pp. 223-224.

F.   APPARATUS AND CHEMICALS

Spectrograph; argon, helium, hydrogen, nitrogen, and mercury discharge tubes; and discharge-tube transformer. (See FIGURES on next page.)
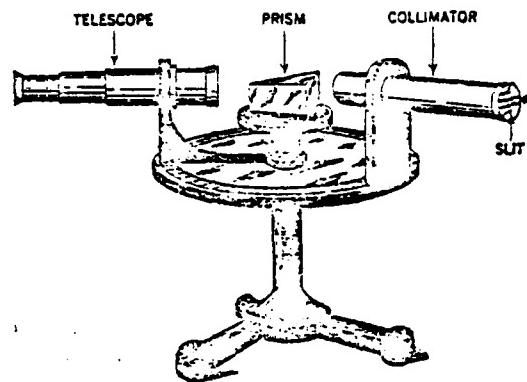
FIGURE 14-1: Spectroscope
(Taffel, A., "Visualized Physics," Cxford Book Company,
1959, p. 221)
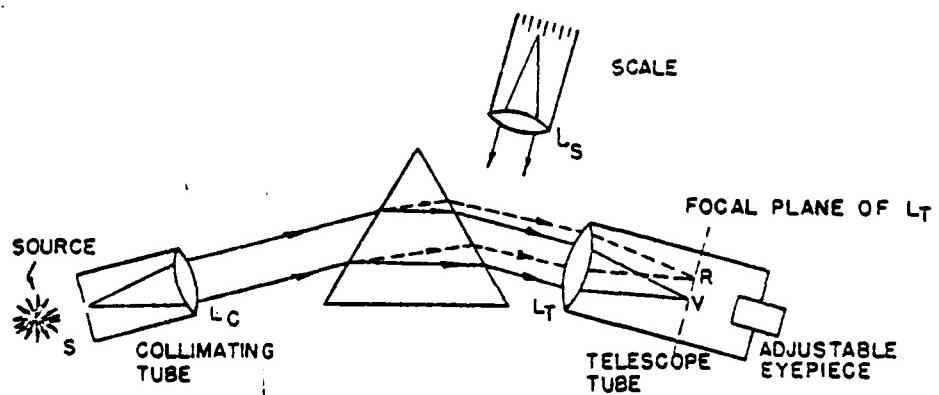
FIGURE 14-2:
(Lindenfeld, P., "Experiments in Physic," Edwards Brothers,
Ann Arbor, Michigan, 1958, p. A1-1)

G. THEORY AND DISCUSSION

The dispersion of light from any given source into a spectrum is studied by means of the spectroscope. This instrument consists of three parts: (1) a collimator, which is simply a tube having a slit at one end and a convex lens at the other; (2) a triangular glass prism; and (3) a telescope. The light source to be examined is placed in front of the slit of the collimator. The collimator then allows a narrow beam of parallel light rays to fall upon the prism, which disperses the light into its spectrum. The telescope is used to magnify the spectrum. A scale is usually attached to the instrument, so that the wave lengths of the colors seen can be measured.

You may have seen that the spectrum produced by a hot incandescent lamp or an arc light is a continuous band of color, ranging from red at one extreme to violet at the other. Such a spectrum is called a continuous spectrum. In general, incandescent liquids and solids give continuous spectra.

If we look at the light coming from a neon sign through a spectroscope, we see that its spectrum is composed of several brilliantly colored lines, separated by large dark spaces. Such a spectrum is called a bright-line, or simply a line spectrum. Each element when in the form of an incandescent gas or vapor has its own characteristic line spectrum, consisting of brilliantly colored lines which only that particular element can produce. Thus, an element may be identified by its line spectrum. This fact has made it possible to identify the elements present in the sun, stars, and other heavenly bodies. When light from such a body is examined in a spectroscope, the line spectra indicate which elements produced the light.

H. PROCEDURE

1. Set up the spectrometer (e.g., Welch Number 3692) in a room that can be darkened. Give very special attention to the instructions. Handle the parts with extreme care. Do not touch the two clear prism or grating faces. Refer frequently to the procedure and warnings. As you set up the spectrometer, keep a record of the operations (for example, adjustments, observations, prism placement). Check with your instructor if you think the telescope axis needs adjustment.

2. Adjust a flashlight or some other white light source in front of the slit, not closer than eight inches. With slit wide open and with prism table covers in place, remove the telescope and project the spectrum onto a white card. If no spectrum can be had, readjust prism position slightly and try again. When the spectrum is discovered, make final prism adjustments so as to produce the brightest and most complete

spectrum (darkest red through dimmest violet) possible. Replace the telescope.

3. Use sodium, mercury, and helium emission lines to calibrate the spectrometer wave length scales. Note the instructions carefully. Follow those instructions, using as primary standard either the mercury green line, sodium D-line, or helium yellow line.

Hg green: 5416 Å, Na yellow: 5890-5896 Å, He Yellow: 5876 Å

Maintain the slit at the narrowest feasible opening. In order to start any discharge tube in operation, first insert it in the stand. With the variable resistor at the lowest possible setting, depress the operation key and advance the Variac until a stable discharge is attained. Release key. Normally, you should operate this tube at no higher voltage. If, momentarily to study a weak line, you wish to use a higher voltage, you may do so for a few seconds at a time. This may be necessary for some of the weak lines. In any case, depress key only while actually observing a spectrum. Do not hold key down longer than 15 seconds at a time when using the helium or hydrogen tubes.

4. When you have adjusted the spectrometer so as to be consistent with two or three of the standard lines, you may catalog the observable lines in the discharge spectra of helium, mercury, and hydrogen. For each line, note:

    a. Color
    b. Apparent intensity
    c. Telescope angle (estimate vernier to 0.05°)
    d. "Instrument wavelength" (The latter observation should be given with limits of error.)

5. The angle scale of the spectrometer may be roughly calibrated by reading the angle corresponding to registration of each set of successive wavelength marks. This calibration curve, which is based on the manufacturer's evaluation of the prism geometry and index refraction at each wavelength, is best plotted as a frequency versus angle graph. Frequency, for this purpose, should be expressed in wavenumbers.

6. Cautions:

    a. Do NOT overheat spectrum tubes.
    b. Do NOT heat spectrometer with a nearby flame.
    c. Do NOT attempt to measure line positions with a wide-open slit.

I. CALCULATIONS

1. Make a primary calibration curve by plotting frequency

of a number of known mercury and helium lines as a function of observed angle. Compare this with the rough calibration curve you have obtained. The rough curve may be useful for interpolation and extrapolation of the primary calibration curve.

2. Read from the primary calibration curves the frequencies of all other observed lines, and catalog all observed lines of each spectrum by frequency, wavelength, and apparent intensity.

3. How could you have obtained some of the same lines as dark-line spectra? Describe an experimental arrangement. Discuss the relative intensities to be expected in dark line spectra. How can you change relative intensities? Discuss the effects of gas pressure in the discharge tubes, of applied voltage, and of electrode spacing upon the bright-line spectra.

4. The Rydberg equation can be expressed as

$$\frac{1}{\lambda} = \bar{\nu} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where λ is the wavelength, $\bar{\nu}$ is the wave number, R is the Rydberg constant, n_1 is an integer, and n_2 is an integer greater than n_1. Plot $\bar{\nu}$ versus $1/n_2^2$ on a graph paper. If the points fall on a straight line, this is a partial confirmation of the equation above.

5. What does the slope of the line in 6 represent? What is its value? Compare with the known value.

6. What calculation can be made to correct for the value obtained in 5?

J. EXAMPLES AND PROBLEMS

Determine the frequency, wave length, wave number, and
energy of several of the possible transitions between energy
levels in the hydrogen atom. (See Figures below.)
(Kemp, 1974, p. 6-16)
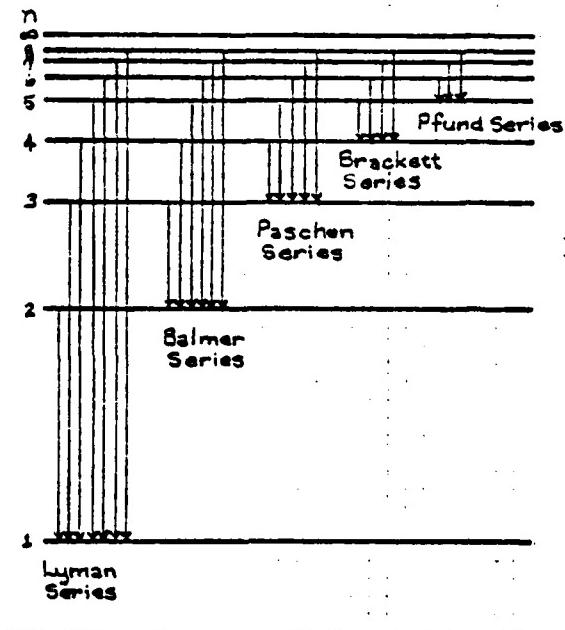
FIGURE 14-3: Energy Levels
of the Hydrogen Atom
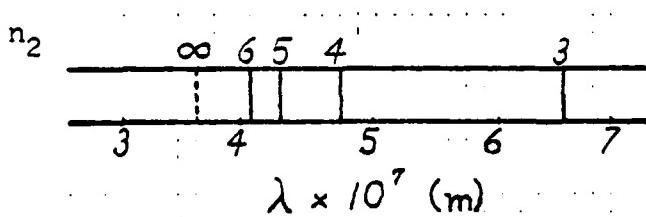
FIGURE 14-4: Emission
Spectrum of the Balmer
Series for the Hydrogen
Atom

EXAMPLE 14-1: Let's go through a sample calculation of the wave number, $\bar{\nu}$, wave length, λ, frequency, ν, and energy, ΔE. Using the figure on the previous page as a reference and the

Rydberg equation, $\frac{1}{\lambda} = \bar{\nu} = R(\frac{1}{n_1^2} - \frac{1}{n_2^2})$, where $R = 1.097 \times 10^5$.

For Lyman series $n_1 = 1$, we will do the calculation for n=2 and n=∞.

----

n = 2

$\bar{\nu} = (1.097 \times 10^5)(\frac{1}{1^2} - \frac{1}{2^2}) = 8.23 \times 10^4 \ cm^{-1}$

$\lambda = 1/\bar{\nu} = 1.22 \times 10^{-5} \ cm = 1220 \ \overset{o}{A}$

$\nu = c/\lambda = \frac{2.998 \times 10^8 \ m\text{-}sec^{-1}}{1.22 \times 10^{-7} \ m} = 2.46 \times 10^{15} \ sec^{-1}$

$\Delta E = h\nu = (6.626 \times 10^{-27} J\text{-}sec)(2.46 \times 10^{15} sec^{-1})$

$= 1.630 \times 10^{-11} \ J$

n = ∞

$\nu = 1.0797 \times 10^5 \ cm^{-1}$

$\lambda = 9.12 \times 10^{-8} \ m$

$\nu = 8.99 \times 10^{16} \ sec^{-1}$

$\Delta E = 5.97 \times 10^{-10} \ J$

The same type of calculations many be made for the Balmer, Paschen, and Brackett series.

EXAMPLE 14-2: Calculate the Rydberg constant, R, for hydrogen and compare it with the accepted value.

Using the values found in your lecture textbook for wavelengths in Balmer region gives the following:

for $\lambda = 6562 \times 10^{-8}$, $n_1 = 2$, $n_2 = 3$, R = 109,722.7

$\lambda = 4861 \times 10^{-8}$, $n_2 = 4$, R = 109,716.8

$\lambda = 4340 \times 10^{-8}$, $n_2 = 5$, R = 109,721.3

$\lambda = 4101 \times 10^{-8}$, $n_2 = 6$, R = 109,722.5

Average R = 109,722.5

R = 109,700 (4SF)

Accepted R = 109,677.6

PROBLEM 14-1: In the Balmer series for atomic hydrogen what is the wavelength of the series limit? (Hint - Consider what happens to $1/n_2^2$ as n_2 approaches infinity.)
(Daniels and Alberty, 1975, p. 430)

ANS: 3647 $\overset{\circ}{A}$

PROBLEM 14-2: What is the mathematical relationship between energy and frequency? What is the frequency called?

PROBLEM 14-3: The yellow doublet of the sodium lamp has an average wavelength of 5893 $\overset{\circ}{A}$. Calculate the energy in
(a) electron volts, (b) kilocalories per mole, and
(c) Joules. (Daniels and Alberty, 1975, p. 430)

ANS: (a) 2.11, (b) 48.7

APPENDIX N

ACID DISSOCIATION CONSTANT OF METHYL RED

APPENDIX N

EXPERIMENT 15:   ACID DISSOCIATION CONSTANT OF METHYL RED

A.   STUDY GUIDE AND REVIEW ASSIGNMENT

1.   Read the appropriate sections of your lecture textbook to obtain an overview of dissociation and absorbance.

2.   Read the THEORY and PROCEDURE sections of this experiment prior to coming to lab.

3.   Supply definitions for the KEY WORDS.   The majority of these are discussed in your lecture textbook.

4.   Complete the PRELIMINARY REPORT of this experiment prior to lab.

5.   Work the following problem to prepare you for the types of calculations you will be expected to make in this experiment:

>   (Daniels, 1975, p. 246)   In order to determine the ionization constant of the weak monobasic acid dimethyl arsinic acid, a solution was titrated with a solution of sodium hydroxide, using a pH meter.   After 17.3 cm^3 of NaOH had been added, the pH was 6.23.   It was found that 27.6 cm^3 was required to neutralize the acid solution completely. Calculate the pK value.

ANS: 6.00

B.   OBJECTIVES - You shall be able to:

1.   Define and/or briefly discuss the KEY WORDS on the next page.

2.   Determine the acid dissociation constant, K, and pK for the reaction in this experiment using a self prepared computer program.

3.   Verify the pK value by plotting $\log\left([A^-]/[HA]\right)$ versus pH.

4.   Describe the use of the spectrophotometric method in c   ulating the dissociation constant.

C. KEY WORDS: (Supply equations where possible based on the equation for the dissociation of a weak acid, $HA = H^+ + A^-$.)

Absorbance

Beer's law

Dissociation constant

Ionization

Molar absorptivity

pH

pK

Spectrophotometrically

Transmittance

Zwitterion

D. PRELIMINARY REPORT - Complete this self-test prior to lab.

1. Why in this experiment is it preferable to calculate pK first rather than K?

2. How do you verify the pK value you obtain from your computer program?

3. Show how EQUATION 15-2 is obtained from 15-1.

4. Why can this experiment be performed using a spectrophotometric method?

5. How do you determine whether or not Beer's law is obeyed?

E. REFERENCES AND SUPPLEMENTARY READINGS - These are references as well as suggestive readings for those students who may wish additional information.

1. Crockford, et al., "Laboratory Manual of Physical Chemistry," John Wiley, New York, 1975, pp. 134-141.

2. Daniels, F., and R. A. Alberty, "Physical Chemistry," John Wiley, New York, 1975, pp. 512-514.

3. Daniels, et al., "Experimental Physical Chemistry," McGraw-Hill, New York, 1970, pp. 113-115.

4. Labowitz, L. C., and J. S. Arents, "Physical Chemistry," Academic Press, New York, 1969, pp. 161-162.

5. Metz, C. R., "Theory and Problems of Physical Chemistry," McGraw-Hill, New York, 1976, pp. 91-92.

6. Salzberg, et al., "Physical Chemistry," Academic Press, New York, 1969, pp. 390-392.

7. Tobey, S. W., _J. Chem. Educ._, 35, 514(1958).

8. Wilson, et al., "Experiments in Physical Chemistry," Pergamon Press, New York, 1962, pp. 98-101.

F. APPARATUS AND CHEMICALS

Spectrophotometer for measuring absorbances in the visible range; pH meter; methyl red; sodium acetate; acetic acid; hydrochloric acid; 95% ethanol; volumetric flasks and pipettes for preparing solutions (See PROCEDURE).

G. PURPOSE

The object of this experiment is to determine an equilibrium constant for a chemical reaction in solution using spectrophotometric measurements.

H. THEORY

In aqueous solution methyl red is a zwitterion and has a resonance structure somewhere between the two extreme forms shown in FIGURE 15-1. The top formula is associated with the red form, HMR, which exists in acid solutions. When base is added, a proton is lost and the yellow anion MR$^-$ is formed as shown by the formula at the bottom of FIGURE 15-1.

Acid form (HMR) red

Basic form (MR⁻) yellow
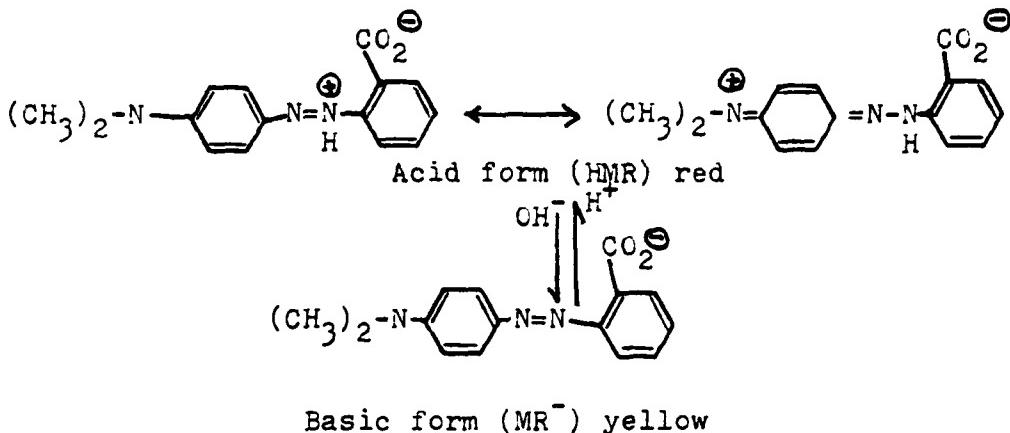
FIGURE 15-1: HMR and MR⁻ forms of methyl red.

The equilibrium constant for the ionization of methyl red is

$$K_a = \frac{[H^+][MR^-]}{[HMR]} \qquad (15\text{-}1)$$

It is convenient to use this equation in the form

$$pK_a = pH - \log\frac{[MR^-]}{[HMR]} \qquad (15\text{-}2)$$

The ionization constant may be calculated from measurement of the ratio $[MR^-]/[HMR]$ at known pH values.

Since the two forms of methyl red absorb strongly in different regions of the visible range of the spectrum, the ratio $[MR^-]/[HMR]$ may be determined spectrophotometrically. The absorption spectra of methyl red in acidic and basic solutions are determined, and two wavelengths are selected for analyzing mixtures of the two forms. These two wavelengths, λ_1 and λ_2 are chosen so that at one, the acidic form has a very large molar absorptivity compared with the basic form, and at the other, the situation is reversed. The molar absorptivities of HMR and MR⁻ are determined at both of these wavelengths, using several concentrations to determine whether Beer's law is obeyed.

Recall that A, the absorbance, is defined by

$$A = -\log I/I_o \qquad (15\text{-}3)$$

I = intensity of light transmitted through solution and

I_o = intensity of light transmitted through solvent.

For the case in which only one solute absorbs at the given wavelength, then

$$A = abc \qquad \text{where} \qquad (15\text{-}4)$$

a = molar absorptivity of absorbing solute,

b = length of light path in cell, and

c = concentration of absorbing solute.

The molar absorptivity depends on the wavelength, temperature, and solvent.

The composition of a mixture of HMR and MR^- may be calculated from the absorbances A_1 and A_2 at wavelengths λ_1 and λ_2 using the equations

$$A_1 = a_{1,HMR}[HMR] + a_{1,MR}{}^-[MR^-] \qquad (15\text{-}5)$$

$$A_2 = a_{2,HMR}[HMR] + a_{2,MR}{}^-[MR^-] \qquad (15\text{-}6)$$

where the a_i values include both molar absorptivities and the constant cell path.

I. EXPERIMENTAL PROCEDURE (Daniels et al., 1970, pp. 113-115)

NOTE: Plot rough graphs of the spectra and of the calibration curve as you work in case more values are needed or some points are questionable.

1. The procedure for this experiment has been described by Tobey (1958). The methyl red is conveniently supplied as a stock solution made by dissolving one gram of crystalline methyl red in 300 mL of 95 percent ethanol and diluting to 500 mL with distilled water. The standard solution of methyl red for use in this experiment is made by adding 5 mL of the stock solution to 50 mL of 95 percent ethanol and diluting to 100 mL with water.

2. The absorption spectrum of methyl red is determined in hydrochloric acid solution as solvent to obtain the spectrum of HMR and in sodium acetate solution as solvent to obtain the spectrum of MR^-. Distilled water is used in the reference cell.

3. The procedure for using the spectrophotometer should be reviewed if necessary.

4. Since the equilibrium to be studied is affected by temperature, it is important that all the spectrophotometric and pH measurements be made at the same temperature. If the cell compartment of the spectrophotometer is slightly above room temperature, the filled cells should be placed in the spectrophotometer just before making the measurements. In order to obtain the best results, the cell compartment should be thermostated.

5. The acidic solution is conveniently prepared by diluting a mixture of 10 mL of the standard methyl red solution and 10 mL of 0.1 $\underline{M}$ hydrochloric acid to 100 mL. The basic solution is conveniently prepared by diluting a mixture of 10 mL of the standard methyl red solution and 25 mL of 0.04 $\underline{M}$ sodium acetate to 100 mL.

6. From the plots of absorbance versus wavelength, two wavelengths are selected for analyzing mixtures of the acidic and basic forms of methyl red. Further spectrophotometric measurements over a range of concentration are made at these two wavelengths with both acidic and basic solutions to check whether Beer's law is obeyed.

7. The solutions are diluted with 0.01 $\underline{N}$ hydrochloric acid or 0.01 $\underline{N}$ sodium acetate, respectively, so that the medium is held constant.

8. In order to determine the ionization constant of the dye, spectrophotometric analyses are carried out on solutions containing 0.01 $\underline{N}$ sodium acetate, a constant total concentration of dye, and various concentrations of acetic acid.

9. The pH values of these solutions are measured at the same temperature as the spectrophotometric measurements. For methyl red it is convenient to use acetic acid concentrations ranging from 0.001 to 0.05 $\underline{N}$.

J. CALCULATIONS

Plots are prepared of absorbance versus wavelength and absorbance versus concentration of dye in acidic and basic solutions a λ_1 and λ_2. The values of the various molar absorptivities are calculated.

The concentrations of the acidic and basic forms of the dye in the various buffer solutions are calculated by using EQUATION 15-5 and 15-6.

EQUATION 15-2 is used to calculate the pK value for the dye. As a means of testing and averaging the data, log [MR⁻]/[HMR] may be plotted versus the pH. An average literature value is 5.05 ± 0.05 for the 25 to 30°C temperature range.

K. SPECIAL INSTRUCTIONS --- Computer Program

The following data should be input into your program: (1) pH, (2) the associated absorbance values, and (3) the molar absorptivity values. (Since the molar absorptivity values are determined graphically, there is little point for including the actual mathematical operations involved in finding the coefficients in the program.)

Your program should compute the concentrations of HMR and MR⁻ and then use these values in conjuction with their respective pH values to compute pK_a. These pK_a values shculd then be averaged and the resulting average pK_a and K_a reported. It would be useful to you for the purposes of spotting inconsistent data to have the computer print out the concentrations and associated pH and absorbance values for each determination.

L. EXAMPLES AND PROBLEMS

EXAMPLE 15-1: (Labowitz & Arents, 1969, p. 161) In an experiment to determine the concentrations of the two substances A and B in a certain solution simultaneously by spectrophotometry the following data were obtained:

	[A]	[B]	Percent Transmitted at $\lambda = 400$ nm	Percent transmitted at $\lambda = 500$ nm
Solution 1	0.001	0	10	60
Solution 2	0	0.005	80	20
Solution 3	unknown	unknown	40	50

Determine the concentration of A and B in solution 3. (Assume b = 1)

$A = -\log T$ $A = abc$

For Solution 1:
At 400nm, $A = \log(1/0.1) = 1.00$; $a_A = 1.00/0.001 = 1.00 \times 10^3$
At 500nm, $A = \log(1/.60) = 0.22$; $a_A^A = 0.22/0.001 = 0.22 \times 10^3$

For Solution 2:
At 400nm, $A = \log(1/.80) = .097$; $a_B = 0.097/0.005 = 19.4$
At 500nm, $A = \log(1/.20) = .699$; $a_B^B = 0.699/0.005 = 140$

For Solution 3:
At 400 nm, $1000\ c_A + 19.4\ c_B = \log(1/0.40) = 0.398$
At 500 nm, $220\ c_A^A + 140\ c_B^B = \log(1/0.50) = 0.301$

Solving the last two equations simultaneously,

$c_A = 0.000368$ mole/liter $c_B = 0.00156$ mcle/liter

PRCBLEM 15-1: Derive an equation to be used if there is no wavelength at which only one form absorbs light. Cutline the procedure to be followed in analyzing solutions. Use this equation to calculate the concentrations of each form of the indicator.

PROBLEM 15-2: (Daniels & Alberty, 1975, p. 525) To test
the validity of Beer's law in the determination of vitamin A,
solutions of known concentration were prepared and treated
by a standard procedure with antimony trichloride in
chloroform to produce a blue color. The percent transmission
of the incident filtered light for each concentration
expressed in microgrms per milliliter, was as follows:

Concentration	% Transmission
1.0	66.8
2.0	44.7
3.0	29.2
4.0	19.9
5.0	13.3

Plot these data so as to test Beer's law. A solution, when
treated in the standard manner with antimony chloride,
transmitted 35% of the incident light in the same cell.
What was the concentration of vitamin A in the solution?

ANS: 2.6 micrograms/mL

PROBLEM 15-3: (Daniels & Alberty, 1975, p. 526) The protein
metmyoglobin and the azide ion (N_3^-) form a complex. The
molar absorptivities of the metmyoglobin (Mb) and of the
complex (C) in a buffer are as follows:

λ	$a_{Mb} \times 10^{-4}$	$a_C \times 10^{-4}$
4900 Å	0.850	0.744
5400	0.586	1.028

An equilibrium mixture in a 1-cm cell gave an absorbance of
0.656 at 4900 angstroms and of 0.716 at 5400 angstroms.
a) What are the concentrations of metmyoglobin and complex?
b) Since the total azide concentration is 1.048×10^{-4} M,
what is the equilibrium constant for

$$Mb + N_3^- = C?$$
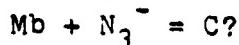
ANS: a) 3.24×10^{-3} M

5.12×10^{-3} $\frac{M}{M}$

b) 2.95×10^4

M. DATA AND RESULTS

1. Determination of Efficient Wavelengths

Acidic Solution			Basic Solution	
λ	Absorbance		λ	Absorbance

2. Beer's Law Confirmation

$\lambda_1 =$ $\lambda_2 =$

T	Acid Soln.	Base Soln.		Acid Soln.	Base Soln.

3. pH and Absorbance Determination

HAc	pH	$\lambda_1 =$	$\lambda_2 =$

4. Average pK =   Average K =

APPENDIX O

LITERATURE SEARCH

APPENDIX O - PART I

SPECIAL ASSIGNMENT---LITERATURE SEARCH IN KINETICS---A REPORT

1. INTRODUCTION

To the chemist the chemical literature serves many nec-
essary purposes. Chemists need to be able to find accurate
physical data quickly or be assured that it does not exist.
They need to be able to find out how a process works, whether
an idea is really new, whether a concept is logical or out of
the question. They need the means to keep up-to-date in their
own specialized branch of chemistry.
In your last laboratory activity in physical chemistry
you will research the literature on one of the following
topics which you will be assigned at random:

1. Hydrolysis of ethylene chlorohydrin and ethylene oxide.

2. Ammonium cyanate-urea conversion.

3. Hydrolysis of β-Lactones.

4. Aldol condensation and cleavage of diacetone alcohol.

5. Nitration of Aromatic compounds. (Pick a system and have
all articles deal with the same system.)

6. Decomposition of di-t-butyl peroxide.

7. Thermal isomerization of α-pinene.

8. Decomposition of nitrogen pentoxide.

9. Hydrolysis of γ-butyrolactone.

10. Bromination of acetone.

11. Phenacyl bromide and pyridine in methyl alcohol.

12. Iodine clock reaction.

13. Oxidation of iodide by persulfate.

*****There are at least 20 articles on each of the above
which you should be able to find.*****

14. If you have trouble finding articles on the above topics,
or if you would like to work on another kinetic system, SEE
YOUR INSTRUCTOR as soon as possible.

II.   OBJECTIVES - You shall be able to:

1.   Become more proficient in using chemical literature.
(For example, the student will be able to locate, read, and
assimilate a journal article.)

2.   Learn more about rate laws, mechanisms and kinetic
theory.

III.   PROCEDURE

1.   As soon as possible start on this research project.   If
you wait until the week before it is due, you may find that
you cannot do it justice.

2.   Four weeks prior to the end of the term you should report
to your instructor with a list of at least 5 references which
you plan to review for this report.

3.   Your references should be from as many diverse sources as
possible.   You may wish to check Mellon's book <u>Chemical
Publications, Their Nature and Use</u> or Woodburn's book <u>Using
the Chemical Literature</u>, for the many types of publications
available.   As a <u>minimum</u> you must cite:

2-Journal articles originally obtained by reviewing Chemical
        Abstracts, such as Journal of Chemical Physics, Journal
        of Physical Chemistry, Journal of Chemical Education,
        or Journal of the American Chemical Society.
1-Article found in specialized comprehensive works such as
        chemical dictionaries or encyclopedias.
1-Article from a review serials type of publication such as
        Chemical Reviews, ACS Monographs, Annual Reviews in
        Chemical Kinetics, or Advances in Chemical Physics.
1-Article from any other source, such books as; Kinetic
        Theory of Gases, Theory of Rate Processes, Chemical
        Kinetics, or kinetics of Homogeneous Gas Reactions.

4.   Your report should include:

        a.   Citations from a minimum of five articles.   Your
        report will be judged in part on your choice of articles.
        Avoid articles which are not sufficiently detailed or
        which do not contain enough experimental work worth
        considering.

        b.   A concise statement of the theory you plan to
        discuss.

        c.   Your review should very briefly outline the problem,
        experimental range of parameters, and results.   <u>Compare</u>
        the treatment and the results of the different articles.
        <u>Do they agree</u>?

d. Comments on the validity of the proposed rate law, mechanisms, or on any assumptions or models that were employed.

e. Any weaknesses and omissions that you detected, if any.

f. Your evaluation of the theory in light of your studies in chemistry.

g. A brief summary together with your critical evaluation of each article reviewed.

h. Finally, in your opinion do these articles represent a worthwhile contribution to the literature.

5. Items 4 a-h constitute the body of the report. This report should be from 3-5 pages in length (type written and double spaced).

APPENDIX O - PART II

SPECIAL ASSIGNMENT---LITERATURE SEARCH IN QUANTUM MECHANICS

1. INTRODUCTION

     To the chemist the chemical literature serves many nec-
essary purposes. Chemists need to be able to find accurate
physical data quickly or be assured that it does not exist.
They need to be able to find out how a process works, whether
an idea is really new, whether a concept is logical or out of
the question. They need the means to keep up-to-date in their
own specialized branch of chemistry.
     However, another very necessary purpose for chemical
literature will be utilized in your last laboratory report
in physical chemistry, i.e., examining the events in the life
of an individual and the development of his concept. You will
research the influences operating and contributions made dur-
ing the period the concept was founded until it was developed
into a theory.
     Your particular assignment will be chosen at random from
the following list:
Compton effect
Heisenberg's Uncertainty Principle
Bohr's Theory of Hydrogen Atom
DeBroglie-Wave Theory
Schroedinger's Wave Equation
Dirac's Theory of the Electron
Classical Hamiltonian function
Planck-Black-body Radiation
Planck's Radiation formula and Planck's constant
Einstein's Photoelectric Effect
Einstein- Average energy of an harmonic oscillator
Dulong & Petit - How quantum mechanics explained the
     deviation in their specific heat law
Debye Model - Deviations from classical theory of equi-
     partition
Rayleigh's Radiation formula
Rydberg's constant
Balmer's formula
Stark effect
Zeeman effect
Pauli' exclusive principle

II. OBJECTIVES - You shall be able to:

1. Become more proficient in using chemical literature.
(For example, the student will be able to locate, read, and
assimilate a journal article.)

2.   Have a better appreciation of the history behind theoretical chemists and physicists.

3.   Understand why one must develop a method of research in theoretical chemistry. Specifically, in the area of quantum theory where for example chemists must develop methods for treating the diverse interactions of light with matter in order to interpret the endless new experiments in chemical physics.

III.   PROCEDURE

1.   As soon as possible start on this research project.   If you wait until the week before it is due, you may find that you cannot do it justice.

2.   Four weeks prior to the end of the term you should report to your instructor with a list of at least 5 references which you plan to review for this report.

3.   Your references should be from as many diverse sources as possible.   You may wish to check Mellon's book Chemical Publications, Their Nature and Use or Woodburn's book Using the Chemical Literature, for the many types of publications available.   As a minimum you must cite:

2-Journal articles originally obtained by reviewing Chemical
      Abstracts, such as Journal of Chemical Physics, Journal
      of Physical Chemistry, Journal of Chemical Education,
      or Journal of the American Chemical Society.
1-Article found in specialized comprehensive works such as
      chemical dictionaries or encyclopedias.
1-Article from a review serials type of publication such as
      Advances in Chemical Physics, Annual Review of Physical
      Chemistry, Review of Modern Physics, Physical Chemistry
      and Advanced Treatise, or Advances in Quantum Chemistry.
1-Article from any other source such as biographical works or
      books such as the History of Quantum Theory.

4.   Your report should include:

   a.   A biographical sketch of the individual and the historical aspects of the period.

   b.   A concise statement of the theory you plan to discuss.

   c.   The origin of theory and the events leading to its pronouncement.

   d.   The development of the theory; comment on any assumptions or models that were employed.

e. The significance of the theory.

f. Your evaluation of the theory in light of your studies in chemistry.

g. A brief summary together with your critical evaluation of each article reviewed. Point out the weaknesses and omissions you may detect in the articles.

h. Finally, in your opinion do these articles represent a worthwhile contribution to the literature.

5. Items 4 a-h constitute the body of the report. This report should be from 3-5 pages in length (type written and double spaced).

APPENDIX P

DETERMINATION OF TRANSFERENCE NUMBERS
BY THE MOVING BOUNDARY METHOD

APPENDIX P

EXPERIMENT 16:   DETERMINATION OF TRANSFERENCE NUMBERS
                 BY THE MOVING BOUNDARY METHOD

A. STUDY GUIDE

1. Read the appropriate sections of your lecture textbook
to obtain an overview of transference numbers.

2. Read the THEORY AND PROCEDURE sections of this
experiment prior to coming to lab.

3. Supply definitions for the KEY WORDS.

4. Complete the PRELIMINARY REPORT of this experiment
prior to lab.

B.   OBJECTIVES - You shall be able to:

1. Define and/or briefly discuss the KEY WORDS.

2. Calculate transference numbers.

3. Calculate ionic mobilities from transference numbers.

C. KEY WORDS: (Supply equations where possible)

Electric mobility

Graphical integration

Ionic conductivity

Ionic mobility

Moving-boundary experiment

Transference number

D. PRELIMINARY REPORT - Complete this self-test prior to lab.

1. How can one calculate the transference number for the anion in solution if you know the transference number of the cation?

2. Why must you be sure that the glass tubing does not contain any air bubbles?

E. REFERENCES AND SUPPLEMENTARY READINGS - These are references as well as suggestive readings for those students who may wish additional information.

1. Baca, G., and R. D. Hill, J. Chem. Educ., 47, 235(1970).

2. Daniels, F., and R. A. Alberty,"Physical Chemistry," John Wiley, New York, 1975, pp. 370-375.

3. Kallo, R. M., and S. Bluestone, J. Chem. Educ., 43, 204(1966).

4. Labowitz, L. C., and J. S. Arents, "Physical Chemistry," Academic Press, New York, 1969, p. 126.

5. Shoemaker, D. P., and C. W. Garland, "Experiments in Physical Chemistry," McGraw-Hill, New York, 1962, p. 186.

F. APPARATUS-The moving-boundary apparatus (See FIGURE 16-1), a
200 V---5mA dc power supply (constant voltage), 1000 ohm decade
resistance box, thermostat at 25 °C, volumetric flasks and
pipette (for dilutions of), 0.100 N HCl solution, methyl violet
indicator, a recording potentiometer, and a cadmium anode and
a Ag/AgCl$_{(s)}$ wire cathode.
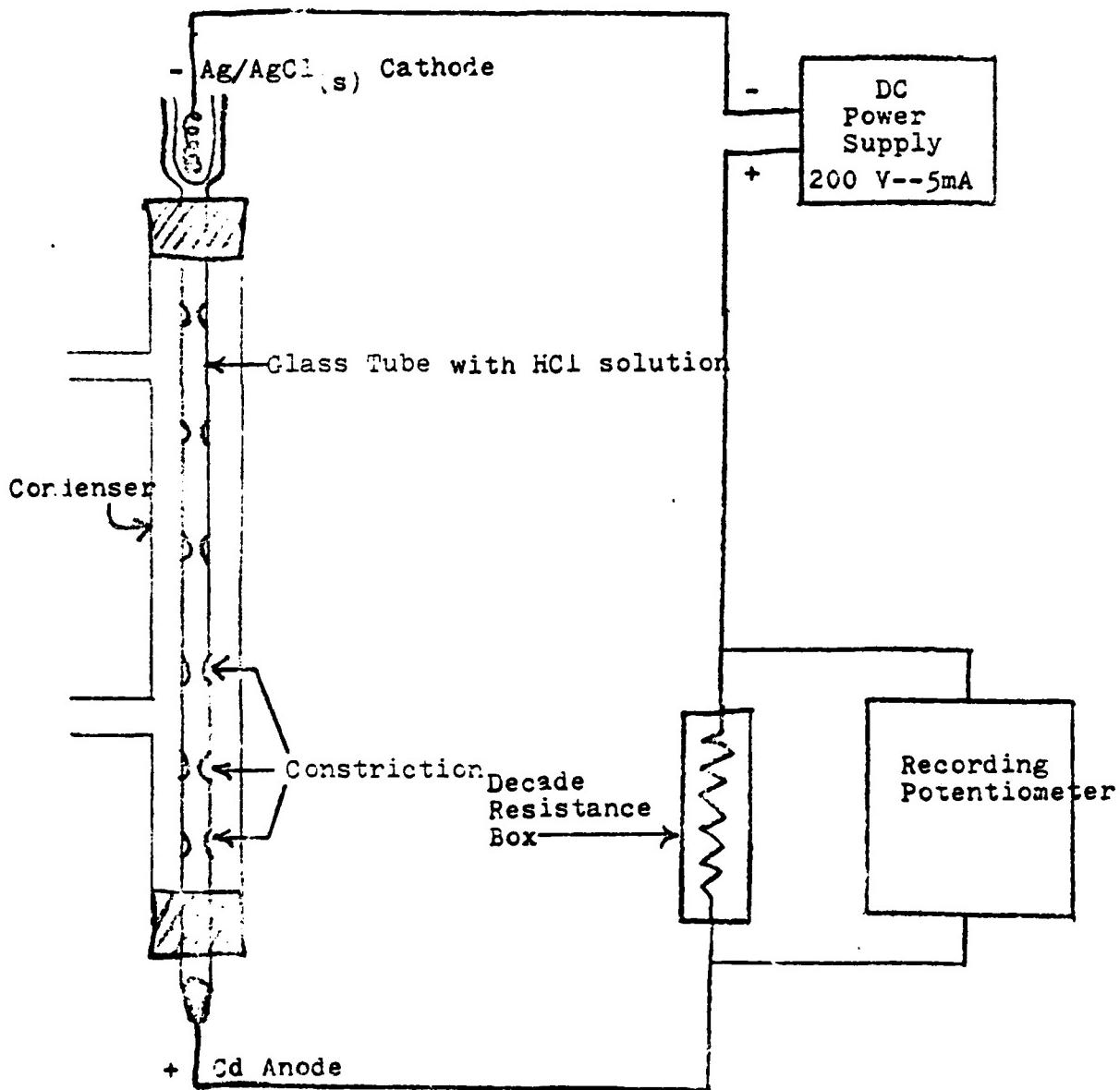
FIGURE 16-1 Moving-boundary Apparatus

G. PURPOSE

The objective of this experiment is to determine the transference numbers of hydrogen and chloride ions in a dilute HCl solution.

H. THEORY

An electrolyte owes its characteristic properties to the presence of ions which result from the dissociation of the substance. In solutions of strong electrolytes most of the original substance has undergone dissociation into ions. When a potential difference is established between electrodes dipping into an electrolyte, positively charged ions, cations, move toward the negative electrode and ions bearing negatively charged ions, anions, move toward the positive electrode. The electric current in solution of electrolytes consists of this migration of ions. It might seem at first glance, that if a cation, hydrogen, were moving toward the cathode it might carry all the electricity. However, only a portion of the current is carried by the hydrogen. That portion is known as the <u>transference number</u> of the hydrogen ion.

In a solution of a strong electrolyte the transference number of the cation may be expressed as T_c. The transference number of the anion may be expressed as T_a. The relationship between T_c and T_a is $T_c + T_a = 1$. Thus for an electrolyte solution, if T_c is calculated T_a is immediately known.

The transference number of an ion depends on temperature, concentration, and the conductance of the other ions present. In experimental physical chemistry, transference numbers furnish information about hydration, complex ion formation, and colloids. The study of colloids by this method is referred to as electrophoresis. Transference numbers are determined by the classical Hittorf method, an emf method, or by the moving-boundary method.

In the moving boundary method, a boundary between solutions with the same anion or cation is subjected to an electric field E. In this experiment Cl^- is the common ion, H^+ and Cd^{2+} are the cations. When a current is initially applied through the HCl solution, cadmium ions leave the cadmium anode. At the silver/silver chloride cathode the primary reaction is

$$2H^+ + 2e^- \longrightarrow H_2.$$
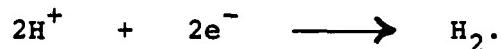
Since this reaction takes place far removed from the boundary area no mixing due to the evolution of hydrogen gas occurs. With the applied current H^+ moves toward the cathode followed by a cadmium chloride ion solution formed autogentically at the anode. A boundary forms immediately which can be seen with the naked eye when the solutions are concentrated. Typically, methyl violet indicator is added to the

HCl solution prior to the experiment to aid in the determination of the boundary. The original boundary may be formed either by a mechanical device or as in this experiment electrochemically by filling a tube with one electrolyte and generation of the other electrolyte at the anode as the current is passed. Once the boundary is formed it will remain sharp as long as current is passed, if the denser solution is at the bottom and the faster moving ion is on top. The sharpness of the boundary results from the change in the voltage gradient at the interface between the solutions. As the faster moving ion pulls away, the region at the interface develops a higher resistance and therefore a higher ohmic drop. This results in a higher voltage gradient, which pulls the slower moving ion along at the same speed as the faster ion.

In general the position of the boundary may be followed by the difference in refractive index or color of the two solutions, or by the addition of a suitable indicator. Both of these methods which have been used in the past lead to results which depend on human judgement. The modification described in the EXPERIMENTAL section minimizes the dependence on human judgement.

In the past the total charge that passes was measured by an external coulometer, or by measuring the current and the time, the current being held constant. This approach required constant monitoring and adjustment of external resistance or a very expensive constant current power supply. The approach utilized in this experiment overcomes that difficulty by the use of a graphical integration technique described in the PROCEDURE section.

As the boundary moves a distance Δx, a corresponding volume V can be determined. This volume can be measured on a graduated pipette or by use of a constricted tube as in this experiment. The hydrogen ion transference number T_H is the ratio of the charge carried by the H^+ to the total charge transferred. The charge carried by the H^+ (Q_H) is equal to the volume times the equivalents per cm^3 times the number of charges per equivalent, the Faraday:

$$Q_H = VcF = \frac{VCF}{1000} \qquad (16\text{-}1)$$

where c = the number of equivalents per cm^3,

C = the number of equivalents per liter = molarity for HCl

F = the Faraday, and

V = the volume in cm^3.

The total charge transferred is

$$Q = \int_{t_o}^{t} Idt \qquad (16\text{-}2)$$

$$T_H = \frac{Q_H}{Q} = \frac{VCF}{1000} Q \qquad (16\text{-}3)$$

Q is determined by substituting Ohms law into (2), I = E/R:

$$Q = \frac{1}{R} \int_{t_o}^{t} Edt \qquad (16\text{-}4)$$

A plot of E vs. t is obtained by recording the voltage dropped across a known resistor on a chart recorder. The integral is evaluated by cutting out and weighing the area under the curve of E vs. t, or a planimeter may be used to integrate the area under the curve.

T_{Cl^-} can be found by using

$$T_H + T_{Cl} = 1. \qquad (16\text{-}5)$$

As an additional part of the experiment, the specific conductance of the solution may be calculated first. From the value of the specific conductance and the value of the transference number, ionic mobilities can be calculated. Ionic mobility u is defined as the ratio of the ion velocity to the electric field gradient:

$$u = \frac{VL}{Q}, \qquad (16\text{-}6)$$

where, L = the specific conductance.
Substituting this into equation (3) gives

$$T_H = \frac{FCu}{1000} L \qquad \text{or}$$

$$u = \frac{1000 \ L \ T_H}{FC}. \qquad (16\text{-}7)$$

1. EXPERIMENTAL

In the classical moving boundary experiment a 1-mL pipette graduated every 0.1 mL was used. This pipette was placed in a vertical position and at the bottom was placed a metal anode and at the top the cathode. The cathode was normally a Ag/AgCl electrode or a piece of Pt wire depending on the solution to be electrolyzed.

The electrodes are connected to a source of direct current capable of delivering about 5 mA. With this

apparatus it was necessary for the current to be held constant during the experiment. If the applied voltage is constant, the current through the capillary will decrease during the experiment, because as the boundary ascends the tube, the length of the column of electrolyte below the boundary increases and this solution is a poorer conductor than the one it replaces. The potential applied to the cell had to continually be increased. This was normally done by the experimenter by adjusting the current supplied by manually changing the resistance of the external circuit. Since the normal moving boundary experiment takes from 1 to 3 hours per run, this method was very tedious. In addition the student had to watch the boundary and record the time at which the boundary crossed successive graduations on the pipette with the aid of a stopwatch. Not only was this tedious, but the results of the experiment depended on deciding when the boundary had moved across a graduation.

The procedure for this experiment was modified in the form given here. First the pipette was replaced with a piece of glass tubing of uniform inside diameter on which constrictions about 3-5 centimeters apart were made. The constriction distances are not critical, however, the volume between the constrictions must be calibrated as precisely as possible. This can be done either by weighing the volume of mercury that is contained between the constrictions or by use of a salt solution of known transference number which allows the calculation of the volume. Both methods have shown to be in agreement to with + 0.3%.

The above modification alone does not remove the necessity for noting when the boundary passes a given constriction. A second modification accomplishes this determination through the graphical integration technique.

J. PROCEDURE

1. Prepare a 0.5 $\underline{N}$ HCl stock solution, known to three significant figures. From this stock solution make two other solutions of about 0.25 $\underline{N}$ and 0.1 $\underline{N}$, with each concentration known to three significant figures. Add a drop or two of methyl violet indicator to the volumetric flasks prior to diluting to the mark. The indicator serves as an aid in making the moving-boundary visible, but is not necessary using the apparatus designed for this experiment. (THESE PREPARATIONS SHOULD BE MADE PRIOR TO THE LAB TO SAVE TIME.)

2. Set up the moving-boundary apparatus as shown in FIGURE 16-1. Attach the condenser to the thermostat and set to 25°C. This water jacket removes the heat generated by the passage of current.

3. Rinse the tube with the solution to be measured.

4. Attach the cadmium anode to the moving-boundary apparatus. Fill the tube with the solution to be measured making sure that there are no air bubbles. (Air serves as a high resistance to current flow.) One way to do this is with a syringe and capillary tubing. Care must be taken to prevent stirring of the solution by bubbles or thermal convection currents.

5. Put the Ag/AgCl cathode in place. Connect the electrodes to the power supply with the correct polarity. Turn on the power supply.

6. Adjust the decade resistor and recording potentiometer so that there is as large a current as possible resulting in a large area to be under the curve on the chart paper.

7. Record the resistance, voltage range, chart speed of the recording potentiometer, and the concentration of the solution.

8. The current flow may be stopped any time after the moving boundary has passed the fourth constriction. This will take about an hour.

9. Drain the moving-boundary apparatus by removing the anode. Repeat steps 2-9 for the other solutions.

K. CALCULATIONS

Voltage versus time is graphed on the recording potentiometer. A noticeable break in the curve is noted as the solution passes through a constriction. This is due to a large increase in resistance causing a sharp decrease in current. The volume between each constricion must be determined for a given piece of apparatus. For one specific tube the volumes were as follows:

Volume between constrictions

1 & 2	.7457 cm^3
2 & 3	.7414
3 & 4	.7395
4 & 5	.7303
5 & 6	.7536

1. Using the graphical integration technique, cut a square section of the chart paper to be used as a standard. Weigh the chart paper and determine its area. Cut out the piece of chart paper corresponding to the area under the curve. Cut this piece into parts corresponding to the area between the constrictions, and weigh them. Calculate Q from the area under the curve as shown in EXAMPLE 16-1.

2. Using EQUATION 16-3, the molarity of HCl, Q (from step 1), and the volume between the constrictions, calculate the transference number of hydrogen.

3. Using EQUATION 16-5 calculate the transference number of chlorine.

4. Using EQUATION 16-7 and the values given below for the specific conductance, L, calculate the ionic mobility.

5. Compare your values for the transference numbers and ionic mobilities with the following values:

$[H^+]$	L	T_H	Ionic Mobilities cm^2/V-sec
.250	.0892	.838	.0031
.100	.0391	.831	.00332
.050	.01995	.829	.003165
.010	.00416	.825	.0029

These values were obtained from Weissberger, A., "Physical Methods of Organic Chemistry," Interscience, New York, 1959.

L. EXAMPLES AND PROBLEMS

EXAMPLE 16-1: A student is given the following experimental data.

Concentration of HCl is 0.100 M.
Chart speed is 20 mm/min.
The decade resistance is 58.40 ohms.
Chart scale is 1.00 volt for full scale deflection.
The chart paper measures 24.95 cm for full scale.
The weight of the area of the paper under the curve between constrictions 2 and 3 is 2.560 g.
The weight of a standard piece of chart paper is 4.5605 g and its length is 34.87 cm and its width is 24.94 cm.
The volume of the tube between constrictions 2 & 3 is 0.861 cm^3.

Calculate Q, T_H, % error in T_H, and ionic mobility.

Area of standard square is 34.87 x 24.94 = 869.7 cm^2.
The area to weight ratio is 869.7/4.5605 = 169.9 cm^2/g.
The area under the curve is

$$2.560 \text{ g} \times 169.9 \text{ } cm^2/g = 486.1 \text{ } cm^2$$

Using the chart speed and length for full scale deflection gives

$$486.1 \text{ } cm^2 \times \frac{1 \text{ volt}}{24.95 \text{ cm}} \times \frac{1 \text{ min}}{2.0 \text{ cm}} \times \frac{60 \text{ sec}}{1 \text{ min}} = 584.5 \text{ V-sec.}$$

By EQUATION 16-4,

$$Q = \frac{1}{R} \int E dt$$

$$Q = \frac{584.5 \text{ V-sec}}{58.40 \text{ ohm}} \times \frac{1 \text{ amp}}{1 \text{ V/ohm}} \times \frac{1 \text{ coulomb}}{1 \text{ amp-sec}} = 10.01 \text{ coulombs}$$

By EQUATION 16-3, $T_H = \dfrac{VCF}{1000 \ Q}$

$$T_H = \frac{(.861 \text{ cm}^3)(.100 \text{ eq/cm}^3)(96,485 \text{ coul/eq})}{1000(10.01 \text{ coulomb})} = 0.830$$

% error $= \dfrac{.831 - .830}{.831} \times 100 = 0.12$ %

By EQUATION 16-7, $u = \dfrac{1000 \ L \ T_H}{FC}$

$$u = \frac{1000(.0391 \text{ ohm}^{-1}\text{-cm}^{-1})(.830)}{96,485 \text{ V-sec/ohm-eq}(.100 \text{ eq/cm}^3)} = .00336 \text{ cm}^2/\text{V-sec}$$

% error $= \dfrac{.00336 - .00332}{.00336} \times 100 = 1.3$ %

PROBLEM 16-1: (Daniels & Alberty, 1975, p. 381) A moving-boundary experiment is carried out with a 0.1 $\underline{M}$ solution of HCl at 25°C (Specific conductance = 4.24 ohms^{-1} m^{-1}). Sodium ions are caused to follow the hydrogen ions. Three milliamperes is passed through the tube of 0.3 cm^2 cross-sectional area, and it is observed that the boundary moves 3.08 cm in one hour. Calculate (a) the hydrogen-ion mobility, (b) the hydrogen-ion transference number, (c) the chloride-ion mobility, and (d) the electric field strength.

ANS: (a) 3.63 x 10^{-7} m^{2}v^{-1}s^{-1}, (b) 0.826,
(c) 7.64 x 10^{-8} m^{2}v^{-1}s^{-1}, (d) 23.6 V m^{-1}

PROBLEM 16-2: (Labowitz & Arents, 1969, p. 126) Longsworth determined the transferece number of the sodium ion in 0.0200 $\underline{M}$ NaCl at 25°C by the moving boundary method and obtained the following data:

Distance traveled by boundary, cm 0 1.00 6.00 10.00

Time, seconds   0 344   2070 3453

The cathode was Ag/AgCl and the anode was Cd. The cross-sectional area of the tube was 0.1115 cm^2. The current was 0.0016001 amp. Calculate the transference number of the sodium ion under these conditions.

ANS: $T_H = 0.390$

APPENDIX Q

WRITING A COMPUTER PROGRAM FOR THE TREATMENT
OF A PARTICLE IN A ONE-DIMENSIONAL BOX

APPENDIX Q

EXPERIMENT 17: WRITING A COMPUTER PROGRAM FOR THE TREATMENT
        OF A PARTICLE IN A ONE-DIMENSIONAL BOX

A. STUDY GUIDE

1. Read the appropriate sections of your lecture textbook
to obtain an overview elementary quantum theory.

2. Read the THEORY and PROCEDURE section of this experiment.

3. Supply definitions for the KEY WORDS.

4. Complete the PRELIMINARY REPORT to obtain an idea of
some of the things your program should be able to do.

B. OBJECTIVES - You shall be able to:

1. Define and/or briefly discuss the KEY WORDS on this
page, including equations.

2. Write a computer program to solve for E, ψ, and ψ^2.

3. Write a computer program to plot ψ versus x, and ψ^2
versus x.

4. Apply the equations associated with the particle-in-a-box.

C. KEY WORDS: (Supply equations where possible.)

Dimension of box for the particle-in-a-box problem, x

Frequency of radiation (s^{-1} = Hz), ν

Mass of a particle, m

Planck's constant, $6.626176(36) \times 10^{-34}$ J s, h

Potential energy of a system, V

Principle quantum number, n

Speed of light, c

Total energy of the system, E

Wavefunction that describes the state of the system, ψ

Wavelength ($\overset{o}{A} = 10^{-10}$m), λ

Schrödinger equation

D. PRELIMINARY REPORT

1. What is the wavelength associated with a ball having a mass equal to 5.0×10^{-2} kg and a velocity of 35 m/s?

$$\text{ANS: } 3.8 \times 10^{-34} \text{ m}$$

2. Calculate the mass of a particle having a wavelength of 8.2×10^{-12} m and a velocity of 2.4×10^{3} m/s.

3. Determine the energy of the first two energy levels for a nitrogen molecule constrained to a box 0.10 m on each side. (Hint: You only have to solve for one dimension.) Compare theses energies to RT at room temperature.

$$\text{ANS: } 1.18 \times 10^{-41} \text{ J}$$
$$4.71 \times 10^{-41} \text{ J}$$
$$\text{negligible}$$

4. For a particle-in-a-box, find the probability of finding the particle between $a/4$ and $3a/4$ for $n=2$.

$$\text{ANS: } \tfrac{1}{2}$$

NOTE: Your program should be able to calculate the answers to numbers 3 and 4 above.

E. REFERENCES

1. Daniels, F. and R. A. Alberty, "Physical Chemistry," John Wiley, New York, 1975, pp. 400-403.

2. Kemp, M. K., "Physical Chemistry for Engineering and the Physical Sciences: A Self-Paced Approach," Marcel Dekker, New York, 1974, pp. 6.22-6.31.

F. THEORY

Prior to the start of this century many scientists believed that an electron behaved as a particle. In 1923 de Broglie suggested that matter itself might have some wave character. He proposed that particles should have a wave length associated with them. A particle of mass m, should have a wave length of

$$\lambda = \frac{h}{mv}$$ (17-1)

where v is the velocity of the particle and h is Planck's constant. Later others observed the diffraction of electrons; a definite wave behavior. However, light behaves as a wave at times and as a particle at others. Matter behaves as particles at times and as waves at others. This emphasizes the duality of nature. Such duality was the source of much consternation for a long time but is now accepted as a fundamental property of nature.

What we observe depends on the method we use for observing. Certain types of measurements reveal the particle behavior while others reveal the wave behavior. The observation of wave behavior of electrons quickly produced the development of wave or quantum mechanics. In 1926 Erwin Schrödinger and Werner Heisenberg independently developed a new kind of mechanics - wave mechanics. The formulations of the two are very different but they yield consistent results. They both assume some wave-like nature for particles.

Schrödinger's method is based on an equation and a set of rules that allow characterization of the behavior of matter, particularly in systems in which a particle is restricted to regions with the dimensions of atoms and molecules. This method is the counterpart of Newton's laws of motion. Newton's laws, which are always presented without any derivation of the fundamental principles or proof, let one calculate the mechanical behavior of objects of baseball and even planetary size. Schrödinger's equation is likewise presented without derivation of the fundamental principles or proof and is of particular interest in chemistry because it is applicable to the behavior of objects down to molecular and atomic (but probably not subnuclear) dimensions.

The best way to approach the development of the Schrödinger wave equation is to accept it as a postulate. Schrödinger developed his wave equation by making an analogy between the wave properties of matter and the wave behavior of a vibrating string. The analogy is not complete in that the final result cannot be derived. One must make use of the postulates of quantum mechanics. (See the applicable section of your test and/or reference 2.)

The Schrodinger equation in three dimensions is

$$-\frac{h^2}{8\pi^2 m} \nabla^2 \Psi + V\Psi = E\Psi \qquad (17\text{-}2)$$

where V is the potential energy function of the particle
which will be a function only of coordinates, and where

$$\nabla^2 = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2},$$ and Ψ is the wave function

describing the system.

In most texts study of the Schrodinger equation typi-
cally deals with particles restricted to movement in one
dimension. For such a particle, the potential energy is a
function of this one dimension, which can be taken as being
along the x axis and can be represented by V(x). The in-
formation which will go into the Schrodinger equation in a
particular problem will be the nature of V(x) and the mass m
of the particle. The information which we attempt to obtain
is the allowed values of the energy of the particle and the
relative probabilities of the particle's being at various
positions along the x axis. Solutions of the Schrodinger
equation are a function of x and are denoted by $\Psi(x)$ or
simple Ψ, which is called the wave function for the particle.
No actual physical significance can in reality be applied to
Ψ, however, the square of Ψ is related to the relative
probability of the particle's being in various regions along
the x axis.

The Schrodinger equation in one dimension is

$$-\frac{h^2}{8\pi^2 m} \frac{d^2\Psi}{dx^2} + V(x)\Psi = E\Psi \qquad (17\text{-}3)$$

The behavior of a particle is represented in quantum mechanics
by this function Ψ. Satisfactory solutions of Ψ will gener-
ally exist only for certain values of the allowed energies of
the particle, E. The probability function Ψ^2 is readily
obtained from Ψ.

Consider a particle confined to a square-well potential-
energy function as shown in FIGURE 17-1.
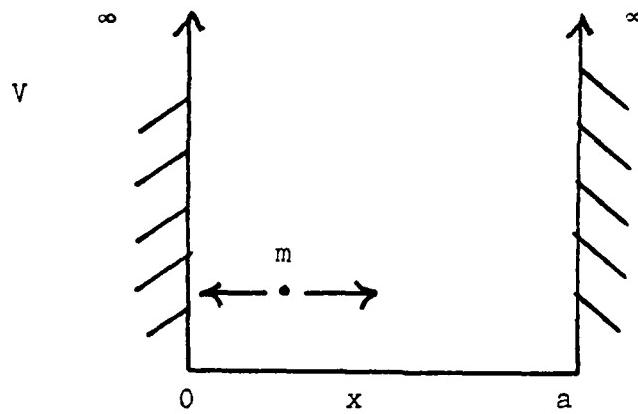
FIGURE 17-1: Potential Energy Diagram

Between x=0 and x-a the potential energy has a constant value of zero (V(x) = 0). Outside this region, for x<0 and x>a, the potential energy of the particle is taken as infinitely high, resulting in a zero probability of finding the particle in that region. Since Ψ^2 must be zero for x<0 and x>a, Ψ must be zero in these regions. Since the potential energy function is V(x) = 0 in the region 0<x<a, the Schrödinger equation reduces to

$$- \frac{h^2}{8\pi^2 m} \frac{d^2\Psi}{dx^2} = E\Psi. \qquad (17\text{-}4)$$

Rearranging this produces a second order differential equation that can be solved

$$\frac{d^2\Psi}{dx^2} = - \frac{8\pi^2 mE}{h^2} \Psi. \qquad (17\text{-}5)$$

A possible function whichsolves the differential equation and also satisfies the boundary conditions is given by

$$\Psi = A\sin\frac{n\pi x}{a} \qquad \text{where } n = 1, 2, 3, \ldots. \qquad (17\text{-}6)$$

and A is what is known as a normalization, which can be shown to be equal to $A = (2/a)^{\frac{1}{2}}$ (17-7)

This value of A results in making the total probability of finding the particle between 0 and a equal to unity.

Thus $\Psi = (\frac{2}{a})^{\frac{1}{2}}\sin\frac{n\pi x}{a}$ (17-8)

is a solution of EQUATION 17-4 and the associated allowed energies are given by

$$E = \frac{n^2 h^2}{8ma^2}. \qquad \text{where } n = 1,\ 2,\ 3,\ \ldots. \qquad (17-9)$$

The allowed energies E are quantized, i.e., can only have certain values due to the quantum number n.

    The fact that the allowed energy can only have discrete values is important. In quantum mechanical problems, the imposition of boundary conditions as illustrated above re- sults in the appearance of the quantum numbers that appear in the energy term. This is the source of the term quantum mechanics - the energies of the system are quantized, that is they can have only certain values.

    FIGURE 17-2 is a plot of the wave function Ψ and the probability density function Ψ^2 for the lowest energy level corresponding to the case where n = 1.
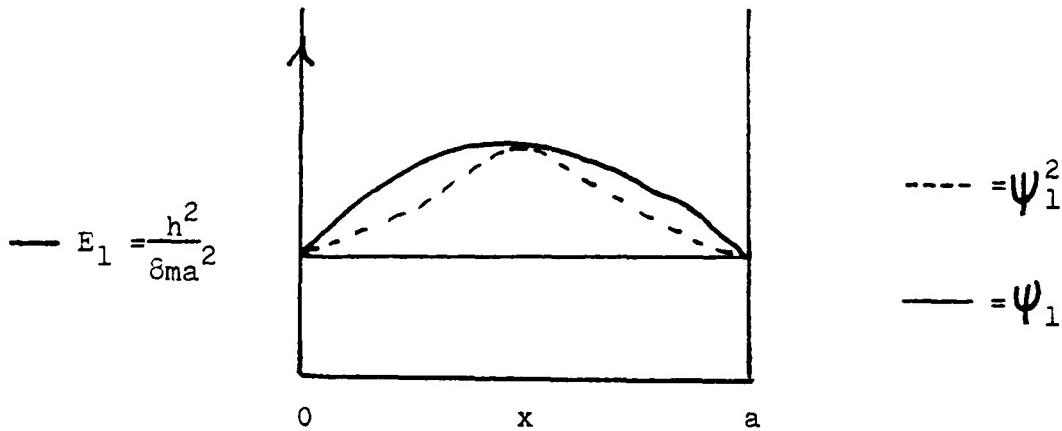

FIGURE 17-2: Wave function Ψ, and the probability function Ψ^2, for first allowed energy level, i.e., for n = 1.

There are a few important features you should note. As the mass of the particle is increased, the spacings of the energy levels becomes closer and closer together. If the mass becomes large enough for the quantity ma^2 to be much larger than h^2, then the energy levels appear to be continuous since they become so close together. Only when ma^2 is on the order of h^2 do quantum mechanical results show up. See EXAMPLE 17-1 for a feel for the sizes involved.

G. PROCEDURE

This experiment is different in that you have the opportunity to design the procedure yourself. Using your knowledge of programming you are to write, test, list, and provide a detailed run showing what can be done using your program. The following is an outline of the minimum requirements. Your instructor may add or modify them as necessary. Using EQUATIONS 17-4, 5, 6, 7, 8, & 9:

1. Pick typical values for the mass, m, and quantum number, n, and allow them to be input. In the output, the values of m and n should be printed. Choose appropriate values for the length of the box, a, and input them.

2. For the printed values of m, a, & n, print the values of Ψ, Ψ^2 and corresponding values for x. Thus x must be input.

3. For the above values of m and n, calculate and print the values for the energy, E.

4. Have your program plot Ψ versus x, and Ψ^2 versus x.

5. Label all variables that are output by your program...

This program will hopefully give you a feeling for the variables contained in the Schrödinger equation. You should understand the principles in the PRELIMINARY REPORT questions, EXAMPLE 17-1, and PROBLEM 17-1. They represent the type of problems that your program should be able to solve.

H. EXAMPLES AND PROBLEMS

EXAMPLE 17-1: (Kemp, 1974, p. 6-31) Calculate the energy between the levels $n = 1$ and $n = 2$ for the following:

a. A 50 g golf ball on a 100 meter fairway.

b. An α particle (He nucleus) moving in a 10 m accelerator tube.

c. An electron in a 1.54 $\overset{\circ}{A}$ bond.

----

a. $E_1 = \dfrac{n^2 h^2}{8ma^2} = \dfrac{(1)^2 (6.626 \times 10^{-34} \text{ J-s})^2}{8(0.050 \text{ kg})(100 \text{ m})^2}$

$= 1.097 \times 10^{-70} \text{ J}^2\text{-s}^2\text{-kg}^{-1}\text{-m}^{-2} = 1.097 \times 10^{-70} \text{ J}$

$E_2 = 4(E_1) = 4.388 \times 10^{-70} \text{ J}$

b. $E_1 = 8.26 \times 10^{-44} \text{ J}$

$E_2 = 4(E_1) = 3.30 \times 10^{-43} \text{ J}$

c. $E_1 = 2.68 \times 10^{-18} \text{ J} = 1.61 \times 10^6 \text{ J/mole}$

$E_2 = 4(E_1) = 6.44 \times 10^6 \text{ J/mole}$

Only in case c are the energy level spacings significant. At room temperature

$RT = 2.48 \times 10^3 \text{ J/mole}$

so the energies involved for small particles confined to small spaces are significant.

PROBLEM 17-1: A very useful exercise for you at this point is to plot the form of the wave function for the next three or four energy levels as was done in FIGURE 17-2, for $n = 1$. The abscissa will be the dimension of the box, 0 to a. Also, on the same plot, show the form of the function ψ^2. You will see how the probability function changes with n.

APPENDIX R

THE PHOTOELECTRIC EFFECT

APPENDIX R

EXPERIMENT 18: THE PHOTOELECTRIC EFFECT

A. STUDY GUIDE AND REVIEW QUESTIONS

1. Read the sections of your physical chemistry lecture textbook about Planck's theory and the photoelectric effect. This will give you a short overview of these theories.

2. Work the following problem prior to coming to lab:

(Daniels and Alberty, 1975, p. 430) An experiment on the emission of photoelectrons from a sodium surface by light of different wavelengths gave the following values for the potentials at which the photoelectric current was reduced to zero. Plot voltage against frequency, and calculate (a) the threshold frequency and (b) Planck's constant.

λ,A	=	3651	3125
E,V	=	-0.950	-0.382

ANS: (a) 10.5×10^{14} s^{-1},   (b) 6.58×10^{-34} J s.

3. Read the THEORY and the PROCEDURE sections of this experiment prior to coming to class.

4. Supply definitions for the KEY WORDS. The majority of these terms are discussed in the THEORY section and in your lecture textbook.

5. Complete the PRELIMINARY REPORT prior to performing the experiment.

6. If possible read the applicable "Operating Instructions" in the Instructor Manual for your monochromator.

B. OBJECTIVES - You shall be able to:

1. Define and/or briefly discuss the KEY WORDS.

2. Determine the threshold frequency of a phototube.

3. Determine Planck's constant.

4. Determine the work function for a given phototube.

5. Understand the causes of the photoelectric effect.

C.   KEY WORDS: (Supply equations where possible.)

Frequency, ν

Kinetic energy, KE

Mercury lines

Monochromator

Planck's constant, h

Photoelectric effect

Photons

Quanta & quantized

Stopping potential, V_s

Threshold frequency, ν_o

Threshold wavelength, λ_o

Wavelength, λ

Work function, θ

D.   PRELIMINARY REPORT - Complete this self-test prior to lab.

1.   What safety precaution needs to be taken in this experiment.

2.   What is the relationship between kinetic energy and the stopping potential?

3.   How are wavelength and frequency related?

4.   What is the purpose of the monochromator in this experiment?

5.   What, if any, is the physical significance of Planck's constant?

6.   What is the photoelectric effect?

E. REFERENCES AND SUPPLEMENTARY READINGS - These are
references as well as suggested readings for those students
who may wish additional information.

1. Cardona, M., and L. Ley, "Photoemission in Solids I,"
Springer-Verlag, New York, 1978, pp. 1-31.

2. Daniels, F. and R. A. Alberty, "Physical Chemistry,"
John Wiley, New York, 1975, pp. 390-392.

3. Kemp, M. K., "Physical Chemistry for Engineering and
the Physical Science," Marcel Dekker, New York, 1974,
pp. 6.8-6.10.

4. Lobkowicz, F., and A. C. Melissinos, "Physics for
Scientists and Engineers," Saunders, Philadelphia, 1975,
pp. 444-445 and 518-525.

5. Schaum, D., "Theory and Problems of College Physics,"
McGraw-Hill, New York, 1961, pp. 237-241.

6. Sutton, R. M., "Demonstration Experiments in Physics,"
McGraw-Hill, New York, 1938, pp. 488-495.

7. Wall, C., R. B. Levine, and F. E. Christensen, "Physics
Laboratory Manual," Prentice-Hall, New Jersey, 1972,
pp. 307-309.

F. APPARATUS AND CHEMICALS

Light-tight box containing phototube, mercury-vapor lamp,
potentiometer, 2 dry cells (lantern type work well),
nanoammeter, digital voltmeter, and either Kodak Wratten
filters #22, 24, 25, and 29 (or similar) or a monochromator.
The potentiometer should be about 100 ohms or a combination
of two potentiometers can be used one for course the other
for fine adjustments. (See the diagram in PROCEDURE section
for setting up the apparatus.)

G.   THEORY

Before getting into the theory of the photoelectric effect one can demonstrate the photoelectric effect by this simple demonstration.   To a gold-leaf electroscope attach a freshly sandpapered zinc leaf.   Charge the electroscope leaf positively and then determine the rate of leak, first without the zinc being illuminated by light and then again with the piece of zinc being illuminated with ultraviolet light (mercury-vapor lamp).   There should be no significant difference.   Now charge the leaf negatively and repeat the experiment.   It should be found that there is a great increase in the leak rate when the leaf is illuminated with light. This demonstrates electrons are leaving the leaf under the action of light.   Furthermore, if the path between the light source and the negatively charged zinc metal is interrupted by a glass plate which is not transparent to ultraviolet light the leak rate is appreciably reduced.   However, if a quartz plate is used (quartz is transparent to ultraviolet light), there is again a large increase in the leak rate. This shows that for zinc the effect is due to ultraviolet light.   You will be doing a similar experiment and you will calculate the threshold frequency, the frequency below which no electrons will be emitted from the surface or a metal when in contact with a light source.

The experimental facts given above are among the strongest evidence for our present-day belief that the electromagnetic radiation is quantized.   It must be assumed that the radiation consists of "quanta" of energy.   In addition, the the energy of these quanta are related to the frequency of the radiation (light) by the Planck equation

$$E = h\nu \tag{18-1}$$

where E is the energy of the quantum, ν is the frequency of the radiation, and h is a proportionality constant given by Planck as h = $6.6262 \times 10^{-34}J$ s.   These quanta are called photons.

Albert Einstein in 1905 developed a similar equation to Planck's during his studies of the photoelectric effect.   The photoelectric effect or photoelectric emission is associated with the observation that when light below a certain wavelength is projected onto an active metal surface electrons are ejected.   The kinetic energy of the ejected electrons is related to the frequency of the incident of light above the threshold frequency.   These observations were first made by Heinrich Hertz, in 1887.   Hertz also observed that the number of electrons ejected was proportional to the intensity of the beam and that there is no time lag between the incidence of light and the emission of   electrons.

The total energy of the ejected electron is the sum of the energy binding it to the metal, θ = eW; where e is the charge on the electron, where θ is

called the <u>work function</u>; and the kinetic energy due to its velocity, that is,

$$E = \tfrac{1}{2}mv^2 + \theta. \tag{18-2}$$

This is Einstein's famous photoelectric equation applying the Planck concept and resolving the difficulties of the wave picture of light. He proposed that the light incident on the surface is made of discrete units or quanta, each with an energy $h\nu$. This packet of energy is totally absorbed by the electron with no allowance for division of the energy between electrons. Einstein's formula becomes

$$h\nu = \tfrac{1}{2}mv^2 + \theta. \tag{18-3}$$

This equation immediately explains many observations. If the frequency of the light is below a threshold value, ν, there will be no electrons emitted since there is not enough energy to overcome the binding energy holding the electrons to the metal. Greater intensity just means more quanta are available so more electrons are released but they all will have the same energy since all the quanta have the same energy.

The fact that the value of h required by Einstein's equation is the same as that found in Planck's equation was powerful support for Planck's theory. From this foundation has grown the whole edifice of quantum theory.

Equation 18-3 has been extensively verified for many materials and over a broad range of frequencies. What is experimentally measured is the energy of the emitted photo-electrons as a function of frequency. A simple way of doing this as is done in this experiment is by way of a retarding potential technique. The electrons are bound to the surface with varying energies, but the binding energy of the last tightly bound electrons depends on the material of the emitter. The energy required to remove these least tightly bound electrons is called the <u>work function</u>, θ, of the metal. Since the work function is usually not known beforehand, the kinetic energy of the photoelectrons, $E = KE = \tfrac{1}{2}mv^2$, is obtained as a function of ν so that the slope of the straight line

$$E = h\nu - \theta \tag{18-4}$$

yields h, and the intercept at the extrapolated point $\nu = 0$, can give θ. When a <u>retarding potential V</u> is used to measure E, we have $E = eV$, so that really it is the ratio h/e that is determined

$$eV = E = h\nu - \theta, \quad \text{or} \tag{18-5}$$

$$V = (h/e)\nu - \theta/e, \tag{18-6}$$

where θ = eW. Only light above a certain minimum frequency can do this, thus the existence of a photoelectric threshold. The threshold frequency is that which is just sufficient to eject an electron with no kinetic energy. Thus the threshold frequency ν_o is given by the relation

$$h\nu_o \ = \ \theta \ = \ eW. \qquad\qquad (18-7)$$

Below this threshold frequency the incident photons will not have sufficient energy to release even the least tightly bound electrons, no matter how intense the light.

The peaks of emission current occurring at different light frequencies come about because of selective absorption. Therefore, some phototubes have peak outputs for light in the infrared region of the spectrum, some in the ultraviolet region, and some in the visible region.

The arrangement generally used consists of a clean surface of the metal to be investigated, and an anode facing or surrounding the cathode, both sealed in vacuum. When radiation is incident on the cathode, electrons are emitted which reach the anode giving rise to a detectable current if the circuit between anode and cathode is completed through a sensitive current meter. If a negative potential V is applied to the anode, only electrons with E > eV can reach the anode, and for some potential V_o no electrons at all arrive at the anode. This stopping potential multiplied by e is equal to the energy of the fastest electrons emitted. In practice all electrons are not emitted with the same energy, and therefore the threshold at V_o, is not very sharp.

In this experiment one can determine the threshold frequency of a phototube, Planck's constant, the work function
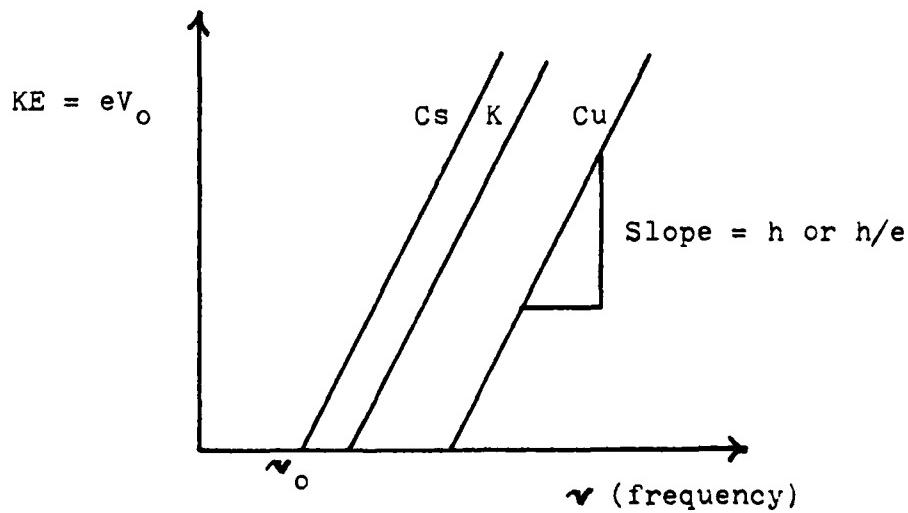

FIGURE 18-1: Millikan's Experiment

of the phototube, and the kinetic energy of the emitted photo-
electrons. It is also possible to determine the frequency of
light, the intensity of the light source, the photoelectric
current, and the chemical identity of the surface from which
the photoelectrons emerge. For instance, Millikan's experi-
ment showed that a plot of kinetic energy versus frequency
of light produced straight lines of the same slope for dif-
ferent metals, but different threshold frequencies
(FIGURE 18-1).

H.   EXPERIMENTAL PROCEDURE

1. Assemble the apparatus listed in the APPARATUS section.
A source of monochromatic light is needed. A Jarrell-Ash
0.25 meter Ebert monochromator works very well. Any photo-
tube operating in the visible range should work. The follow-
ing phototubes have proven successful: an RCA #929, a Bausch
& Lomb Cetron, CE-A59RX (taken from a Spectronic 20), or a
Leybold company catalog # 55877 type phototube. Coaxial leads
should be used in making the connections. A sensitive current
detecting device such as a Model MV-852-A picoammeter is needed
as well as a voltage measuring device such as a NLS series
LX-2 digital voltmeter. A light source is needed. A mercury-
vapor lamp works well, but a sodium lamp or any other light
source may be used. This procedure will assume the use of a
mercury-vapor lamp.

2. Connect the components as shown in FIGURE 18-2 and
FIGURE 18-3. The photocurrent is measured with the ammeter
connected to the photoanode. The cathode is connected to the
potentiometer controlled variable DC voltage which provides
the desired retarding or accelerating field. Arrange the
lamp so that the light passes through the monochromator.

CAUTION: Care must be excercised in using the mercury source
since it also transmits ultraviolet light which can seriously
damage the eyes and cause sunburn to the skin.

Use the following mercury line color scheme for identifying
the exact wavelength and thus corresponding frequencies. The
mercury lines most readily available are

  Yellow at 5780 $\overset{\circ}{\mathrm{A}}$ (Doublet)

  Green at 5461 $\overset{\circ}{\mathrm{A}}$

  Blue at 4358 $\overset{\circ}{\mathrm{A}}$

  Violet at 4047 $\overset{\circ}{\mathrm{A}}$

Care must be taken that the incident radiation contains only
the line chosen for the investigation. This is one reason
for using the mercury-vapor lamp. Depending on the phototube
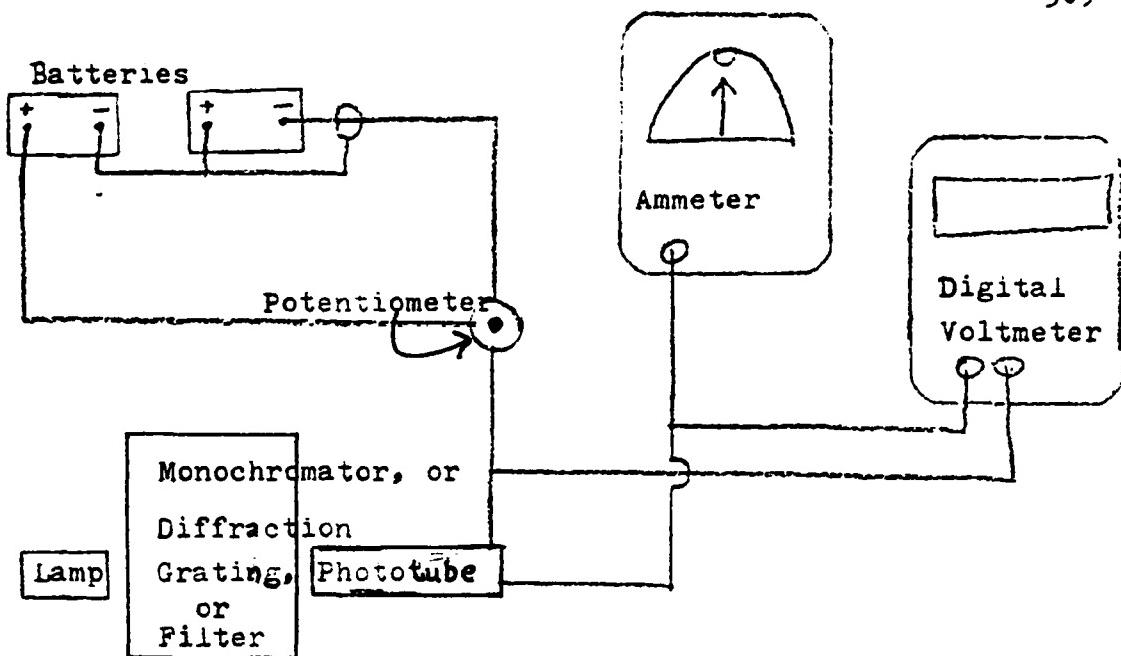
FIGURE 18-2: Experimental Setup
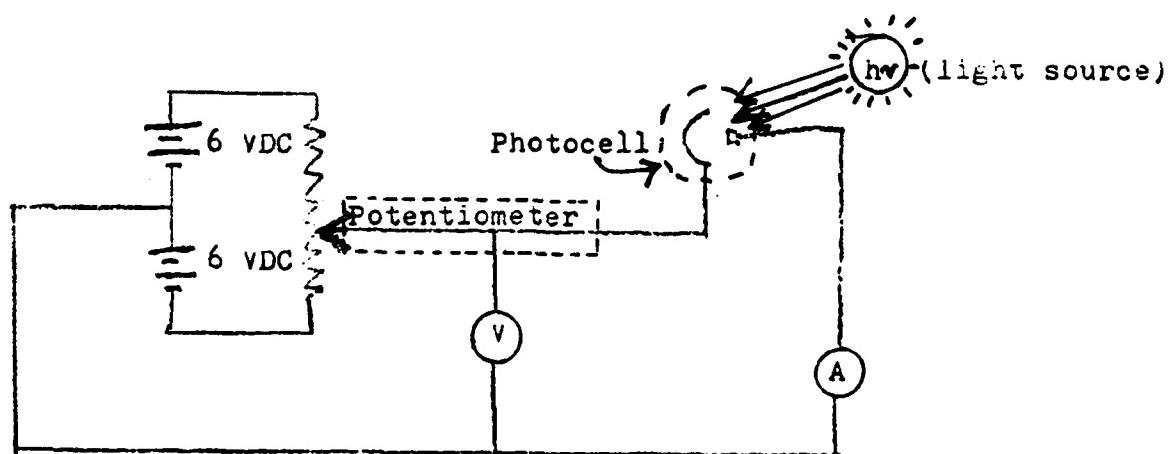
FIGURE 18-3: Circuit Diagram

used, a mask may have to be placed in front of the phototube if the anode is in the path of the light beam and the cathode.

3. Choose one of the above lines and adjust the lamp and phototube to obtain a maximum photocurrent with the potentiometer adjusted to give a maximum reading on the voltmeter. Then with the appratus fixed in place, adjust the monochromator for a maximum deflection on the ammeter. Slowly change the accelerating voltage to a retarding voltage until zero current is obtained and beyond that point until the current levels off at some negative value. This procedure is the most critical and should be repeated two separa · times for each mercury line chosen. The voltage adjustment is made by turning the potentiometer. Record the voltage as the stopping potential at the point at which the current curve just begins to rise. If you are consistent in your method at all frequencies chosen, your results should be good.

4. When the anode potential is sufficiently negative the most energetic photoelectrons are stopped from reaching the anode. For this situation as explained in the theory section we may set $\frac{1}{2}mv^2$ in equation 18-3 equal to eV, and obtain

$$eV = h\nu - \theta \qquad \text{or} \qquad V_s = (h/e)\nu - \theta/e$$

where V_s is the stopping potential. Record the stopping potential for the selected frequencies and plot a graph of V_s versus ν.

I. CALCULATIONS (See EXAMPLES AND PROBLEMS section)

1. Calculate the frequencies corresponding to the wavelengths of the mercury lines.

2. Perform a least squares fit of your data.

3. From the least squares fit of your data determine the slope of the curve, h/e, and then the value of h.

4. Compare your value of h to the accepted value for Planck's constant.

4. Determine the intercept of the line, i.e., the work function of the cathode in both electron volts and joules.

6. From the value of the work function, calculate the value of the threshold frequency, ν_o. (Depending on the individual phototube ranges between 7000 - 11000Å.)

J. ALTERNATE PROCEDURE:

If one does not have access to a monochromator or a diffraction grating one can still obtain results within an order of magnitude of Planck's constant through the use of precise narrow band filters such as the Kodak Wratten filters described in the APPARATUS section.

I. EXAMPLES AND PROBLEMS

EXAMPLE 18-1: The following data was obtained by a student at the USAF Academy for a phototube contained in a Bausch & Lomb Spectronic 20 (Cetron, Ce-A59RX phototube with a S-1 response). From this data calculate Planck's constant, the threshold frequency, and the work function for the alkali metal cathode.

Wavelength, λ, in $\overset{o}{A}$	5461	4358	4047
Frequency, ν, in Hz x 10^{14}	5.493	6.884	7.413
Stopping potential, V_s, in Volts	.70	1.20	1.50

By plotting V_s versus ν, or by using a least squates fit, for the equation $V_s = \frac{h}{e}\nu - \frac{\theta}{e}$, one obtains a value for the slope of 4.05×10^{-15} V s.

$$h = 4.05 \times 10^{-15} \text{ V s}(1.6 \times 10^{-19}\text{Coul}) = 6.48 \times 10^{-34} \text{ J s}$$

which compares very well with 6.65×10^{-34} J s.

Also from the plot or least squares fit, the y-intercept, the work function, $\theta = 1.54$ eV.   When $V_s = 0$, $h\nu_o = eW$,

$$\nu_o = \frac{(1.6 \times 10^{-19})(1.54)}{(6.65 \times 10^{-34})} = 3.70 \times 10^{14} \text{ s, or}$$

$\lambda_o = 8097 \overset{o}{A}$ which is in agreement with the values given in the Bausch & Lomb operations catalog.

EXAMPLE 18-2: The kinetic energies of photoelectrons range from zero to 4.0×10^{-19} J when light of 3000 $\overset{o}{A}$ falls on a surface. Calculate the stopping potential, V_s.

Since the electrons at the surface will have the maximum kinetic energy, KE, for any light frequency, $KE = \frac{1}{2}mv^2 = eV_s$, where V_s is the stopping voltage.

$$V_s = \frac{4.0 \times 10^{-19}}{1.6 \times 10^{-19}} = 2.5 \text{ V}.$$

EXAMPLE 18-3: What is the threshold wavelength for the material in Example 2?

$$eV_s = h\nu - eW_o = \frac{hc}{\lambda} - \frac{hc}{\lambda_o}$$

$$2.5 = \frac{6.65 \times 10^{-34}(3.00 \times 10^{10})}{1.6 \times 10^{-19}}(1/3000 \times 10^{-8} - 1/\lambda_o)$$

$$\lambda_o = 7530 \overset{o}{A}$$

EXAMPLE 18-4: What is the work function of potassium metal if the photoelectric threshold wavelength is 5620 $\overset{o}{A}$?

From $V_s = \frac{h}{e}\nu - \frac{\theta}{e}$, as explained in the THEORY section, the threshold frequency is that which is just sufficient to eject an electron with no kinetic energy. That is when $KE = \frac{1}{2}mv^2 = eV_s = 0$, and $\theta = eW_o = h\nu_o = \frac{hc}{\lambda_o}$.

$$\theta = \frac{6.65 \times 10^{-34}(3.00 \times 10^{10})}{5620 \times 10^{-8}}) = 3.55 \times 10^{-19} J,$$

or, 3.55×10^{-19} J $(1 eV/1.6 \times 10^{-19}$ J$)$ = 2.22 eV

PROBLEM 18-1: If the threshold wavelength for a material is 6000 $\overset{o}{A}$, what is the value of the work function in J & eV?

ANS: 3.33×10^{-19} J, 2.08 eV

PROBLEM 18-2: (Schaum, 1961, p. 239) Will photoelectrons be emitted by a copper surface, of work function 4.4 eV, when lighted by visible light?

ANS: $\lambda = 2820 \overset{o}{A}$, No

PROBLEM 18-3: (Kemp, 1974, p. 6-20) The following data is from R. A. Millikan's determination of threshold energy (binding energy). From this data determine the threshold frequency, threshold wavelength, the work function of the cathode and Planck's constant.

Electron KE (in J) x 10^{-19}	Frequency, v, (in Hz^{-1}) x 10^{14}
3.41	9.58
2.56	8.21
1.95	7.40
1.64	6.91
.75	5.49

ANS: $v_o = 4.32$ x 10^{14} sec^{-1}, $\lambda_o = 6940$ Å, $\theta = 1.79$ eV, and

$h = 6.56$ x 10^{-34} J s

APPENDIX S

PART 1

University of Northern Colorado
College of Arts and Sciences
Department of Chemistry
Greeley, Colorado 80639   January 23, 1977

Dear Sir:

     I am working on a curriculum research project at the
University of Northern Colorado. In this project I am
attempting to develop a more effective physical chemistry
laboratory experience in which the experiments are designed
to teach physical chemistry principles.

     To this end I am soliciting comments from experts in
the field in the form of a questionnaire. I know and
appreciate how valuable a professor's time is. However, I
am sure you also value improvement. In any event, the
questionnaire should not take more than a couple minutes of
your time.

     For your convenience and hopefully to aid in the prompt
return of the questionnaire I have enclosed a stamped self-
addressed envelope. Thank you for your time and effort in
assisting me in this research.

                 Sincerely,

                 Ronald E. Watras
                 Instructor U.S.A.F.Academy
                 Doctoral Candidate at U.N.C.

PART 2

LIST OF COLLEGES TO WHICH QUESTIONNAIRE WAS MAILED

Adams State College
Air Force Academy
University of Arizona
Brigham Young University
California State University, San Jose
Carnegie Mellon
Colorado College
Colorado School of Mines
University of Colorado, Boulder
University of Colorado, Colorado Springs
Colorado State University
Denver University
University of Miami
University of Illinois, Chicage Circle
Lafayette College
Lehigh University
Naval Academy
University of Nebraska
University of North Carolina
Northern Michigan University
University of New Hampshire
Purdue University
Rutgers University
Seton Hall
Texas A & M
U.S. Military Academy, West Point
University of Utah
University of Washington
Washington State University
Weber State
University of Wyoming

PART 3

TC: The Head of the Undergraduate Physical Chemistry
Laboratory Courses.

This is a questionnaire designed to collect data about
undergraduate physical chemistry laboratory courses.

1. Is the physical chemistry laboratory a separate course?
   Yes_____   No_____

2. How many semesters/quarters of P-chem laboratory are
required?
   One quarter_____   Two quarters_____   Three quarters____
   One semester_____ Two semesters_____ Other_____

3. Do you require your students to use one of the major
P-chem laboratory texts (i.e., Shoemaker)?
   Yes_____   No_____

4. If so, what is the text's author? _____

5. If the answer to number three is yes, do you use
supplemental materials?
   Yes_____   No_____

6. If number five is yes, please describe the kinds of
materials used (i.e., Experiments from J.Chem.Ed.).

7. If you do not require the use of one of the major labor-
atory texts, what materials make up your curriculum?

8. How satisfied are your students with the materials you
use?
   Very satisfied_____   Satisfied_____   Unsatisfied_____
   Very unsatisfied_____

9. Would you be in favor of the P-chem laboratory taking
the place if possible of selected topics normally presented
in lecture? Please comment!

10. How could P-chem laboratory be made more effective?

11. How many experiments are required per term___total___?

PART 4

RESULTS OF QUESTIONNAIRE

1. Is the physical chemistry laboratory a separate course?

    Yes 19   No 7

2. How many semesters/quarters of P-chem laboratory are required?

      1 quarter 1
      3 quarters 3
      1 semester 8
      2 semesters 13
      other - $\frac{1}{2}$ semester 1

3. Do you require your students to use one of the major P-chem laboratory texts?

    Yes 19   No 7

4. What's the author of the text?

      Shoemaker et al. 13
      Crockford, Nowell et al. 2
      Daniels et al. 2
      Shoemaker & Daniels 1
      choice of Shoemaker or Daniels 1

5. If you use a major P-chem lab text, do you use supplemental materials?

    Yes 19   No 0

6. If number five is yes, please describe the kinds of materials used (i.e., Experiments from J. Chem. Ed.).

      Experiments designed by faculty 7
      Modified experimental handouts from texts 6
      Experiments from J. Chem. Ed. 6
      Radioisotope Technology book by Chase & Rabinowitz 2
      Experiments from Colloid Chemistry 1
      Experiments from J. Chem. Eng. Ed. 1
      Laboratory Separates 1
      Experiments from White & from Salzberg 1
      Experiments from other texts 3
      Experiments from other schools 1
      References on reserve in the library 1

7. If you do not require the use of one of the major laboratory texts, what materials make up your curriculum?

> Our own lab manual adapted from modifications of
> fairly standard experiments 3
> Writeups developed here are distributed to the students.
> Some are based on experiments in standard texts 2
> In house prepared manual 1
> Reproduced hand-outs and references on reserve in the
> library 1

8. How satisfied are your students with the materials that you use?

> very satisfied 3
> satisfied 21
> unsatisfied 1
> very unsatisfied 0

9. Would you be in favor of the P-chem laboratory taking the place if possible of selected topics normally presented in lecture? Please comment!

> Yes 2
> No 13
> Perhaps 2
> For a well-equipped P-chem lab with a small number of
> students - Yes 1
> We use the lab to supplement the lecture 3
> The treatment of lab experiments is not normally
> sufficient to substitute for lecture 2
> We treat topics lightly in lecture and heavily in lab 1
> I don't understand the question 1
> No - important material should be in both 1

10. How could P-chem laboratory be made more effective? Please describe.

> With more money for updated instrumentation & T A's 7
> With student research projects 3
> By making experiments open ended and by encouraging
> students to devise their own procedures for additional
> lab work 3
> By screening, revising, or eliminating experiments
> which are outdated or poor instructional material 2
> By integrating with analytic & organic courses 2
> By increasing the application of computerized data
> reduction methods 2
> By having a trained person keep apparatus in top work-
> ing condition at all times 2
> Computers 2
> More money and time 2
> More individualized instruction 1

If an instructor remained responsible for the course
for an extended period of time 1
If the lab and the lecture could go hand in hand 1
By spending more time on actual experimentation and
less time on write-ups 1
By using oral exams for experiments and giving lab
practical exams 1
By running the P-chem lab one semester after the
lecture 1
Better experiments 1
More emphasis on basics 1
Modern equipment 1

11. How many experiments are required per term? 5 - 15
How many experiments are required total? 5 - 20
For those schools that had two semesters of chemistry
the average was 8 experiments per semester and 15 total.

12. What is the current enrollment of P-chem lab?

15, 15, 20, 60, 73, 100
This question was not asked of all schools. The average
class size has, however, not changed much over the
years and is between 7 - 45 students. The number of
students seems to be of primary concern in deciding on
whether a self-paced course is feasible.

APPENDIX T

PART 1

P-CHEM LAB QUESTIONNAIRE I   NAME:_____

Please help us to evaluate the P-Chem laboratory:

1. Were the last three labs significantly different from
the Victor Meyer experiment? How?

2. Do you feel that it is necessary to spend 3 weeks on
programming?

3. In regard to what has been expected on the last four
labs concerning treatment of errors, do you feel the
"Treatment of Errors Unit" prepared you sufficiently?
If not, what should be done to improve the Unit, e.g.,
more problems?

4. What did you find most valuable about the last 3 lab
write-ups? Least valuable?

5. What needs to be expanded further? Shortened?
(e.g. theory, procedure, problems, Examples, etc.)

6. The main objective of P-Chem Lab is to try to teach
concepts in the laboratory! Did the last Unit meet this
objective?

7. Is there any way in which this objective can be better
met?

8. Please add any other comments! Does the lab complement
the lecture? Does it have to complement the lecture?

Thank you

Dr. James, Ron Watras, Steve Bunck, Rich Pickwick

PART 2

RESULTS OF QUESTIONNAIRE 1

On question 1 the students unanimously agreed that the last three labs were significantly different from the Victor Meyer experiment. Ways in which the students found the labs different were:
> they were more pertinent to the lecture,
> they were better developed theoretically,
> they dealt with the topic more directly,
> they were more sophisticated with revealing data,
> problems helped in understanding the lab,
> the lab write-ups were more explicit,
> the lab write-ups were more time consuming and harder.

On question 2, half of the students said it was necessary to spend three weeks on programming, while one fourth of the students said the time spent on it was too long, and the other fourth were uncertain.

On question 3, half of the students felt that the "Treatment of Errors Unit" prepared them sufficiently. Improvements suggested by the students were:
> more problems and better explanations
> more equations and more class instruction

The one individual who stated that the Unit was too time consuming was the same individual who wanted to do the least possible.

On question 4, what the students considered most valuable about the last three lab write-ups were:
> the problems,
> their understanding of P-chem concepts,
> and the data sheets

What they found least valuable were:
> error analysis
> the problems were hard to understand.

On question 5, the students that wanted an expanded version wanted the expansion to be in the areas of theory, problems, and examples with a small percentage of the students suggesting changing some problems and examples to match the labs. There was only one request for shortening from the students, and the student requesting it wanted the labs shortened.

PART 2-Continued

On question 6, 86% of the students felt that the
last Unit met the main objective of the P-chem lab of
teaching concepts in the laboratory while 14% of the
students felt that the last Unit did not meet the main
objective.

On question 7, students felt that the objective
could be better met through
more individual help
explaining hard concepts more
cutting down on labs and giving the time to theory
and concepts of the experiment
spending more time on some labs and less on others

On question 8, 75% of the students said that the lab
didn't have to complement the lecture while 25% of the
students felt that the lab should complement the lecture.

What can be concluded from this questionnaire?
1. It appears that these labs are an improvement
over previous labs, especially in the area of teaching
physical chemistry concepts and the addition of examples and
problems.
2. The examples still need to be expanded to a
larger number treating difficult problems in more detail.
3. The problem section needs to include more
concept type questions in addition to the numerical types of
problems.
4. A study guide needs to be incorporated into each
experiment.
5. A majority of the students are willing to learn
from laboratory experiments without having discussed a
given topic in the lecture part of the course. Thus, the
lab does not have to complement the lecture.

PART 3

P-CHEM LAB QUESTIONNAIRE II   WINTER 1977

ELECTROCHEMISTRY

Return this questionnaire as part of your laboratory write-up for Experiment 7.

1. This topic was introduced without previous discussion in lecture. Which word best describes your attitude about the way the Unit was presented?

Favorable__Satisfactory__Undecided__Unsatisfactory__
Unfavorable__

2. Do you feel it was necessary to include electrochemistry as part of the overall P-chem laboratory course?

        Yes_____   No_____

3. Would you have learned as much about electrochemistry concepts if only a lecture presentation had been given and no laboratory activities?

        Yes_____   No_____

4. Did this set of experiments try to teach electrochemistry concepts?

        Yes_____   No_____

5. What changes would you like to see included in any revision of this Unit?

6. How can the laboratory instructor be of more help?

7. Please add any other comments!

Thank you

Dr. James, Ron Watras, & Steve Bunck

PART 4

RESULTS OF ELECTROCHEMISTRY QUESTIONNAIRE

1. This topic was introduced without previous discussion
in lecture. Which word best describes your attitude about
the way the Unit was presented?

        Favorable   1
        Satisfactory   7
        Undecided   1
        Unsatisfactory   2
        Unfavorable   0

2. Was it necessary to include electrochemistry as part of
the overall P-chem lab course?

        Yes   11
        No   0

3. Would you have learned as much about electrochemistry
concepts if only a lecture presentation had been given and
no laboratory activities?

        Yes   2
        No   9

4. Did this set of experiments try to teach electrochemistry
concepts?

        Yes   11
        No   0

5. What changes would you like to see included in any
revision of this Unit?

        Include a previous lecture on the thermodynamics of
        electrochemistry
        Some mistakes in the Unit write-up could be revised
        Some material was not clear
        The electrical diagram could be illustrated better
        Lab 7 took about 6 hours to complete
        Too much work involved for a 1 credit hour course
        A more useful lab than #6 - perhaps 6 & 7 could be
        combined
        The explanation of the calculations procedure could be
        clarified
        Use one period for lecture and then complete lab time
        for the rest
        Experiments 5 & 6 could have been done in one period

PART 4-Continued

6. How can the laboratory instructor be of more help?

Be as prepared as he expects his students to be
He was very helpful when he was around
He could do the lab for us
I feel Steve was very helpful
The lab was long because a lot of time was taken away
by the lecture beforehand
No way
He's done a super job

7. Please add any other comments!

A good unit - I learned quite a bit.
The experiment was good. I felt I learned something.
I feel the lab manual could have been better written.
What we did in experiments 5 & 6 should have been used
in Experiment 7. Why did we calibrate our calomel
electrode?
I don't care much for an hour lecture before lab begins.
I would have learned the theoretical concepts as much
just from lecture, but wouldn't have seen them in
practice without the lab. Therefore, I might not have
understood them real well then.
I am learning to appreciate the mistakes in the lab
manuals.
I feel that I have gained a basic understanding of
these topics.
The lab write-ups force me to explore the ideas behind
electrochemistry instead of just memorizing equations
and terminology.

PART 5

P-CHEM LAB QUESTIONNAIRE III   Winter Quarter 1977

1. In regard to what has been expected on the labs this quarter concerning treatment of errors, do you feel the "Treatment of Errors Unit" prepared you sufficiently? Explain!

2. What did you find most beneficial about the labs this quarter?

3. What did you find least beneficial about the labs this quarter?

4. Which section needs further revision?   Explain!

5. The main objective of P-Chem Lab is to try to teach concepts in the laboratory! Did the experiments this quarter meet this objective?

6. How can this objective be better met?

7. Please add any other comments!

Thank you.

Dr. James, Ron Watras, and Steve Eunck

Part 6

QUESTIONNAIRE IV---SPRING QUARTER

This questionnaire was part of the literature search

project that the students were asked to complete on a

separate sheet of paper.

1. Was this a worthwhile project or would you
rather have performed another 2-3 physical chemistry labora-
tory experiments instead? Why or Why Not?

2. Evaluate the physical chemistry laboratory
portion of the course. Describe in some detail the successes
and failures of this lab course.

3. How could the lab be improved? Any other
suggestions?

(The responses to these questions are given on the next
two pages.)

PART 7-LIST OF STUDENT RESPONSES TO QUESTIONNAIRE IV

1. Too much emphasis placed on the details of how the laboratory report is written

2. The laboratory equipment was not set up or not functioning

3. The results of the experiments were not always as predicted or not very accurate

4. Graphing techniques are not needed since they are taught in mathematics courses

5. Replace tedious experiments with others

6. The laboratory portion of the course was good in that it demonstrated the application of principles discussed in the lecture portion of the course

7. The laboratory experiments were not always performed at the same time as they were discussed in lecture

8. The labs helped me understand some of the principles of physical chemistry

9. The laboratory could be improved by performing the same experiments using different techniques

10. A more detailed theory section is needed for some of the more difficult experiments

11. One improvement would be to modernize the experiments

12. The laboratory was adequate

13. New ideas are needed

14. Equipment could not be found

15. The physical chemistry experiments were not always pertinent

16. The laboratory needs to be related to practical applications

17. I complained a lot, but I think I learned a lot due to the extra effort required

18. There was not enough equipment for the entire class to perform the same experiment at the same time

19. The instruction in the laboratory existed to a full degree

20. Thanks for offering this unique opportunity to give constructive suggestions

21. This course is too much work for a one hour class

22. The instructor should have the laboratory ready to go

23. I have not learned anything from the laboratory

24. Having electrochemistry taught only in the laboratory and then being held responsible by ACS test questions is not fair to the student

25. Written laboratory reports every week were too much of an assignment

26. The reports should deal more with analyzing results and less on the theory of the experiment

27. My criticism is in the amount of material required in every report

28. The labs were good experiments that depicted the material being studied

29. The design of the laboratory course is quite satisfactory for teaching fundamentals of physical chemistry

30. The literature research paper was definitely worthwhile

31. The literature search was a waste of time

32. For the most part, the labs seemed relevant to the lecture material

33. The time and effort spent on laboratory reports could have been better spent on studying the lecture material

34. Contunue to demand that the theory write-up be completed prior to performing the experiment in the lab

35. The materials used in this course will be useful and time saving for others

APPENDIX U

ACS Cooperative Test in Physical Chemistry

Table of Percentile Ranks

APPENDIX U

ACS CCCPERATIVE TEST IN PHYSICAL CHEMISTRY
SUBTEST I--THERMCDYNAMICS
FCRM 1973

TABLE OF PERCENTILE RANKS

Based on data from the Fall 1972 and Spring 1973 National
college testing Program.   Percentile ranks for 461 students
in 47 institutions.*   *(See next page)

Scoring Formula	Total Rights Cnly
Max. Possible Score	45
Percentile Ranks	Raw Scores
99	36.5
95	32.7
90	29.5
85	28.0
80	27.0
75	25.8
70	24.6
65	23.8
60	23.0
55	22.1
50	21.4
45	20.9
40	20.3
35	19.4
30	18.4
25	17.7
20	16.8
15	15.9
10	14.8
5	12.4
1	8.8
σ	5.95
Reliability Coefficient**	0.699

**Estimated by the Kuder·Richardson Formula No. 21.

CHARACTERISTICS CF THE GRCUP

The group upon which the norms were based took the test at
the completion of the Thermodynamics portion of a year's
course in Physical Chemistry, which, in almost all cases, is
about one-third of a year. Most students had a laboratory
course either as a part of this course or as a separate
parallel course. All the schools required general chemistry,
general physics and mathematics through calculus as
prerequisites for the course. Thirteen schools specified
organic chemistry as a prequisite while fourteen schools
indicated an analytical prerequisite generally specified as
Qualitative or Quantitative Analysis.

Number of Students		461
Number of Institutions		47
Lecture Hours per Week	Range	3-4
	Mean	3.1
Laboratory Hours per Week	Range	0-8
	Mean	2.7
Sex	Men	78.9%
	Women	21.1%
Year in College	Sophomore	3.1%
	Junior	57.4%
	Senior	34.8%
	Graduate	4.7%
Professional Goals	Chemist of Eng.	45.4%
	Cther Sci. Major	9.4%
	Cther type Eng.	2.4%
	Medical Sciences	28.0%
	Non-science	1.5%
	Undecided	13.3%

REPCRTING INSTITUTICNS

Albright College
American Int. College
Bates College
Baylor Univ.
Bridgewater St. College
Clarion St. College
Concordia College
Denver Univ.
Dickinson College
Emory & Henry College
Erskin College
Geneva College
Gettysburg College
Grinnell College
Hampden-Sydney College
Henderson St. College
Illinois Benedictine College
Johns Hopkins Univ.

Kansas Newman College
Kansas State College of Pittsburg
Lafayette College
Maryland, University of
Miami, University of
Midwestern Univ.
Minnesota, University of
Missouri, University of
Monmouth College
Mount Marty College
Murray State Univ.
Niagara Univ.
North Carolina, Univ. of, at Greensboro
Regis College
Ripon College
Rochester Institute of Technology
St. John Fisher College
St. Xavier College
Salem State College
Samford Univ.
Siena College
State University College at Brockport
Stetson Univ.
Tennessee, Univ. of, at Martin
Texas, Univ. of, at Arlington
Valparaiso Univ.
Western Maryland College
William Jewell College
Xavier Univ., of Louisiana

APPENDIX V

Sample Pop-Quiz

P-Chem Hazing Questions   11/17/76

Name_____Answer only the questions pertaining
                      to your experiment!

I. Bomb Calorimetry

    1. What is a fuse wire correction?

    2. What compound will be used as a standard for
        calorimeter calibration?

II. Heat of Neutralization

    1. How will the base be introduced into the HCl?

    2. During one part of the experiment an electrical
        heater will be used during which time the voltage
        drop across and the current drawn by the heater
        coil will be measured. Using the following symbols
        for the voltmeter, ammeter, heater, and power
        source, show how they should be connected.

$$+\;\text{\textcircled{V}}\;-\qquad+\;\text{\textcircled{A}}\;-\qquad-|\|\|\;+\qquad$$
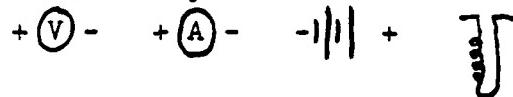
III. Equilibrium

    1. What variables will be plotted in order to
        determine ΔH?

    2. Write an equilibrium expression, K_p, for the
        system being studied.

APPENDIX W

Abstract from the 174th ACS National Meeting

CAN P-CHEM BE LEARNED IN THE LABORATORY? <u>Ronald E. Watras</u>, Department of Chemistry, USAF Academy, Colorado, 80840, and M. Lynn James, Department of Chemistry, University of Northern Colorado, Greeley, Colorado, 80639.

In recent years most new innovations in the teaching of chemistry on the college level have been offshoots of developments started in high school chemistry, e.g., PACE. On the college level many of the programs are along the lines of the Keller Plan. These have been discussed in the Journal of Chemical Education and in the "Proceedings of the Symposium on Self-Paced Instruction in Chemistry." Most of these have been developed for general chemistry lecture and laboratories. To date ther have been few developed for physical chemistry or other advanced course. Those developed for physical chemistry have been primarily concerned with modifying the scheme of instruction presented in lecture. This paper presents a fresh approach concentrating on the content of instruction as has been suggested by some as the next area of concern. The success of implementing a physical chemsitry laboratory course where content is emphasized will be discussed. This includes the case where a physical chemistry laboratory course replaces lectures on some topics, e.g., electrochemsitry, completely freeing the lecture instructor to stress other topics. In other cases the laboratory is used to supplement the material taught in lecture, but still emphasizes fundamental concepts rather than cookbooking an experiment.

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NOTE: The material contained in the first activity,
Data Analysis and Treatment of Errors, is an expanded
modification of the material used by Dr. William Koch,
professor of chemistry at the University of Northern
Colorado. In addition, the theory and procedure sections
of experiments 2 - 14 are modifications of unpublished
experiments used by Dr. Koch at UNC, but developed at the
University of Illinois, Urbana. The theory and procedure
sections for experiment # 15 (Appendix N) are modifications
taken from Daniels et al., 1970, p. 113.

VITA

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